Electric Arc Furnace Oxidation Practice
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The oxidising phase in the refining of steel made in the basic electric arc furnace is discussed, based on published information and practical operating conditions. The effects of hydrogen, nitrogen, sulphur, phosphorus and non-metallic inclusions are briefly reviewed and the adjustment of furnace practice is discussed with a view to the elimination of these elements and inclusions.

THE heavy duties imposed on steel in service to-day demand not only close control over the percentages of alloying elements, but the elimination of impurities, such as hydrogen, nitrogen, sulphur, phosphorus, and non-metallic inclusions. Of the many steelmaking processes, the basic electric arc furnace has proved suitable for making steel as free as possible from these undesirable constituents and to very narrow ranges of analyses. In this steel-making process it is not generally realised that much of the true refining is done during the oxidising period, and by considering published information and practical operating conditions it is proposed to show how this phase of the arc furnace process can be utilised to full advantage. Maximum economy of time, money, and man-power is a necessary factor in the consideration of production, cost and quality for the national effort.

Hydrogen

The effects of hydrogen have yet to be fully investigated, but numerous adverse effects have been observed. Plain carbon steels have their impact resistance reduced and become slightly susceptible to ageing. Steels with less than 0·60% carbon are hot short ; 3% nickel 1% chromium steels become red-short and flaky.[1] Several investigators [2, 3, 4] have reported that steels containing hydrogen are prone to flake formation. If the hydrogen concentration exceeds 0·001%, internal porosity will result because the partial pressure of hydrogen increases during freezing, owing to reduced solubility.[5]

Hydrogen may be present in the charge in ingots or billets rejected for internal porosity, but it usually enters the charge by absorption from the furnace atmosphere. Oily turnings,[6] moist ore and lime,[2, 4, 7, 8] leaky cooling pipes, etc., all cause increased hydrogen in the furnace atmosphere. Acid slags permit less absorption than basic slags,[7, 9] but although a slightly acid slag can be carried during the refining period after slagging-off, it would be inadvisable to attempt this during the oxidation phase. The use of high-melting voltages is thought to accentuate hydrogen pick-up,[6] though this has not been proved.

Most authorities [3, 4, 7, 8, 10] agree that a vigorous boil is necessary for hydrogen elimination. From the equation—

$$2FeO + 2FeH + H_2 \leftrightharpoons 4Fe + 2H_2O \quad [11]$$

the constant for the reaction can be derived.

$$K = \frac{Fe^4 \cdot H_2O^2}{FeO^2 \cdot FeH^2 \cdot H_2}$$

The importance of the concentration of FeO in the metal is obvious. As the product C FeO increases with the rate of carbon removal, [12, 13] the greater the speed of decarburisation, the higher the FeO in the metal for a given carbon content. The FeO in the metal is also inversely proportional to the carbon content [14, 15] for a given speed of carbon removal until the carbon is below 0·12%, when the partition coefficient $K = \frac{(FeO)}{[FeO]}$ exerts a dominating influence. (Square brackets indicate concentrations in the metal, parentheses those in the slag). It is apparent that a rapid boil down to a low carbon content is required for maximum hydrogen elimination. The physical action of the boil is also helpful in sweeping the hydrogen out of the steel.[8] Dehydrogenation is assisted by diluting any hydrogen or hydrogen-bearing gases in the furnace atmosphere by the carbon monoxide evolved during the boil. Limestone in the charge gives off carbon dioxide, which will act in a similar manner. A high residual manganese of between 0·20 and 0·38% is said to be helpful,[2] but the reason for this is obscure.

Nitrogen

Nitrogen is used as a grain-refining alloying element in high chromium cast irons, and imparts hard-wearing qualities to Bessemer steels. In some cases it gives rise to slight ageing effects[10] and causes a brittle range between 800° and 900° C. in Armco iron.[16] Nitrogen is not particularly deleterious, but it must be controlled as occasional casts with high percentages of this element would cause undesirable variations in hardness.

Nitrogen may be present in the charge in high nitrogen high chromium cast iron or in anthracite. Absorption under the arc is the more likely source, especially if it is struck on the bare metal and high voltages are used.[6] Such conditions do occur during the early stages of the melt.

The only known method of removing nitrogen from the metal is by a rapid boil ;[18] this action, which is purely physical, is more effective in eliminating nitrogen than hydrogen.[8] Carbon mon- and dioxide act in the same manner as with hydrogen, according to Sievert's Law, which states that $M = K \cdot \sqrt{p}$, when M = the quantity of gas absorbed, p = the gas pressure, and K is the constant for the gas/metal system and temperature under consideration. Nitrogen also exists in the slag,[19] but no definite (N)/[N] ratio has been established. The percentage in the metal cannot be reduced to less than 0·004, as below

1 Bardenheuer and Keller. *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung.* Vol. 18. 1936.
2 Kuba. *Tetsu-to-Hagane.* October 25. Vol. 23. 1937.
3 Klausting. *Metallurg.* Vol. 12. 1937.
4 Chuyko. *Stal.* Vol. 11. 1938.
5 Chuyko. *Stal.* Vol. 1. 1939.
6 Rassbach. Electrochemical Society. Preprint 77-29.
7 Hofsten, Kalling, Johansson and Knös. *Jernkontorets Annaller.* Vol. 123. 1939.
8 Kobayashi. *Tetsu-to-Hagane.* October 25. Vol. 23. 1937.
9 Belorusov. *Kachestvennaya Stal.* Vol. 9. 1937.
10 Epstein. *Metals and Alloys.* Vol. 6. 1935.
11 Lepp. *Journal of the Iron and Steel Institute.* Vol. 2. 1940.

12 Herty. *Metals and Alloys.* Vol. 1. 1930.
13 Schenk. *Stahl und Eisen.* Vol. 53. 1933.
14 Leiber. *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung.* Vol. 18. 1936.
15 Fetters and Chipman. *Metals Technology.* Vol. 7. 1940.
16 Desch. *Journal of the West of Scotland Iron and Steel Institute.* Vol. 32. 1925.
17 Bonthron. *Jernkontorets Annaller.* Vol. 121. 1937.
18 Bardenheuer and Thanheiser. *Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung.* Vol. 17. 1935.

this figure nitrogen absorption under the arc takes place as fast as it is boiled out.[17]
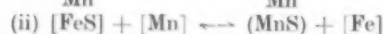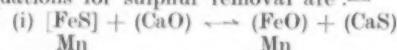
One method of removing dissolved gases from a liquid is to bubble a neutral gas through it. The dissolved gases diffuse into the bubbles of neutral gas as they rise through the liquid. In the case considered, steel is the liquid, carbon monoxide the neutral gas, and nitrogen and hydrogen the dissolved gases. This explanation fits the fact previously mentioned that nitrogen is more easily removed by boiling than hydrogen. The former is present as a dissolved gas and the latter both in solution and as a hydride.

Sulphur

The harmful effect of sulphur on both the mechanical and rolling quality of steel is well known. There is rarely enough of this element present in arc furnace steel to cause any serious trouble in the above categories. Inclusions of any kind are deleterious in high-class steel and sulphur in the form of sulphide inclusions is bad from this point of view alone. This type of inclusion, being conductive, enhances corrosion in aqueous acid solutions and causes pitting of high chromium corrosion-resistant steels.[20]

In the arc furnace process the sulphur comes exclusively from the scrap. The extensive use of high sulphur free-cutting steel increases the average sulphur content of merchant scrap, especially turnings.

The equations for sulphur removal are :—

$$\text{(i)} \quad [\text{FeS}] + (\text{CaO}) \longleftrightarrow (\text{FeO}) + (\text{CaS})$$
$$\text{Mn} \qquad\qquad\qquad \text{Mn}$$
$$\text{(ii)} \quad [\text{FeS}] + [\text{Mn}] \longleftrightarrow (\text{MnS}) + [\text{Fe}]$$

Both products of reaction (i) pass into the slag. The solubility limit of CaS is approximately 4%, but this concentration is not likely to be approached in an arc furnace slag. The removal of FeO and MnO from the slag will help the reaction to proceed from left to right. Transfer of sulphur from steel to slag depends more on the $\text{CaO}/\text{FeO} + \text{MnO}$ ratio than the CaO/SiO_2 ratio.[21] This explains why the reducing slag removes more sulphur than the oxidising slag, though the CaO/SiO_2 of the former may be only two-thirds of the latter. Although the reaction is slightly exothermic, high temperatures aid sulphur elimination by enabling the slag to dissolve more lime and increasing the molecular mobility. A lively boil is helpful, as it greatly increases the slag/metal contact area and aids diffusion of FeS to the scene of reaction. Whether spar is a direct desulphuriser or not is still a debatable point, but it is undoubtedly valuable as a flux, enabling the slag to carry more lime and still retain its fluidity. The surface tension of the slag is, in the author's opinion, very important, but its effect has not been fully investigated.

Reaction (ii) occurs only in the early stages of the melt, as the MnS solubility product is too high at the temperatures encountered later on.[22]

Phosphorus

The bad effects of this element have often been over-stated, and it now finds use in low alloy high-strength constructional steels. There is no doubt, however, that cold shortness and lack of ductility become serious if the phosphorus content of the steel is too high.

As with sulphur, phosphorus comes entirely from the scrap. Cast iron is the most potent source, but this type of scrap is not used in any quantity by the arc furnace trade.

Strongly oxidising conditions are necessary to oxidise the phosphorus in the steel to phosphorus pentoxide, and lime is essential to hold this oxide in the slag as a stable phosphate. The addition of any powerful reducing agent, such as carbon or silicon, will cause the return of phosphorus to the metal. Although the final phase of the oxidising period takes place at high temperature, and this should hinder the strongly exothermic phosphorus reaction, removal of this element continues for the following reasons. The high temperature

and the use of spar enable a highly basic and very fluid slag to be carried, and slag basicity is an extremely important factor in phosphorus elimination.[21] The slag at the end of the oxidation period normally contains over 20% FeO. The vigorous boil promotes the reaction by increasing the physical contact between slag and metal. It seems likely that these considerations outweigh the adverse effects of high temperature on the thermodynamic balance.

Non-Metallic Inclusions

Weldability is impaired by inclusions,[23] and the effect of the sulphide type has already been mentioned under sulphur. By far their worst effect is the lowering of ductility, impact value, and fatigue resistance ; this is especially important in such vital parts as aero crankshafts, connecting rods, etc. Certain types of inclusions must be kept at an absolute minimum in some classes of steel—e.g., stringy silicate inclusions in ball-bearing steel.

Inclusions can roughly be divided into two types, intrinsic and extraneous. The former are deoxidation products and the latter originate from the lander, ladle, and casting-pit refractories. Only the former will be considered here as the oxidation practice will have no influence on the pick-up of the extraneous type.

Silicate inclusions form during the melt by oxidation of silicon present in the scrap. Much research has been done[24, 25, 26, 27, 28] and the only unanimous conclusion is that a boil of reasonable duration is essential. As previously mentioned, the FeO in the metal depends not only on the carbon content, but also on the speed of decarburisation. The $\dfrac{(\text{FeO})}{[\text{FeO}]}$ partition coefficient does not become of primary importance until the carbon is below 0.12%. This is because when the bath is reacting vigorously the equilibrium is between the carbon and FeO in the metal rather than between the FeO in the slag and that in the metal. Temperature has little influence on the C.FeO equilibrium, because although the reaction is endothermic, the heat of solution of FeO in the metal balances it.[29] A rapid boil can be maintained without making any difference to the FeO in the metal immediately before slagging, as this will depend on the $(\text{FeO})/[\text{FeO}]$ ratio if the carbon is low enough.

A high residual manganese is favoured by some people.[27, 30] From the equation $\text{FeO} + \text{Mn} \longleftrightarrow \text{MnO} + \text{Fe}$ the equilibrium constant can be considered as $K = \dfrac{\text{FeO.Mn}}{\text{MnO}}$ all the reactants being in the metal. The MnO is only slightly soluble in the steel and will be precipitated as fine particles. To utilise this as a flux for deoxidation products, the bath manganese must be raised soon before the ferro-silicon addition which is made after slagging-off. The manganese oxidation is exothermic and excessive temperature can cause the manganese to return to the metal. The more usual method is to add ferro-manganese 10–30 mins. before slagging or with the ferro-silicon after slagging. Alternatively, silico-manganese can be used. The lower the melting point of the deoxidation products, the more readily they will coalesce and rise out of the steel. This practice will give a deoxidation product as near as possible to the low melting-point trough in the $\text{FeO}–\text{MnO}–\text{SiO}_2$ system, the ternary eutectic of which melts at 1,170° C.[31] American work[32] has confirmed that FeO and MnO act as fluxes for silica, and that such inclusions are easier to eliminate, as they are fusible and coalesce easily.

Oxidation Practice

The effects, sources and elimination of various elements

19 Eilander and Meyer. *Stahl und Eisen*. Vol. 55. 1935.
20 Portevin and Guitton. *Comptes Rendus*. Vol. 204. 1937.
21 McCance. *Steelmaking Symposium*. Iron and Steel Institute. 1938.
22 Larsen. *Metals Technology*. April. 1941.

23 Blomberg. *Welding Industry*. Vol. 4. 1936.
24 Herty, Fitterer and Christofer. *U.S. Bureau of Mines Technical Publication* No. 492. 1931.
25 Buchholz, Ziegler and Voos. *Report No. 338 of the Steelworks Committee of the Verein Deutscher Eisenhüttenleute*.
26 Myrzyrow. *Metallurg*. Vol. 13. 1938.
27 Halperin. *Metallurg*. Vol. 12. 1937.
28 Fedorov. *Metallurg*. Vol. 11. 1936.
29 Phragmen and Kalling. *Jernkontorets Annaller*. Vol. 123. 1939.
30 Maurer and Voigt. *Stahl und Eisen*. Vol. 60. 1940.
31 Maddocks. *Carnegie Scholarship Memoirs*. Iron and Steel Institute. 1935.
32 Herty and Fitterer. *Transactions of the American Society for Steel Treating*. Vol. 15. 1929.

and inclusions have been reviewed, and it now remains to adjust furnace practice to compromise between the varying and sometimes contradictory requirements.

Limestone should be added in the charge for several reasons. It is cheaper than burnt lime, less likely to contain moisture, has a lower sulphur content, tends to break up easily, does not float about in lumps, and provides an ample supply of carbon dioxide to dilute the nitrogen and any hydrogen in the furnace atmosphere. There is no doubt that a lively boil is necessary, not only to remove hydrogen, nitrogen and non-metallic inclusions, but to increase contact between slag and metal, speeding up the reactions generally. A strong boil will assist melting and prevent undue reflection of the arc on to the roof and side-walls which occurs if the bath is quiescent. If high-carbon scrap is used, ore can be charged to start a reaction before the scrap in front of the door has melted. The prevailing low temperature and the presence of iron oxide during the early part of the melt will favour the oxidation of phosphorus and the lime will hold it as a stable phosphate. If the scrap is light and rusty, carbon must be added in the charge to minimise the danger of melting low in carbon. This would cause wear and tear on the lining by the formation of a thin, highly oxidising slag which would reflect the heat and cut the banks. A good boil is impossible under these conditions unless hæmatite or spiegel is added as a source of carbon. A fairly high residual manganese will help the boil in eliminating silicate inclusions formed by the oxidation of silicon in the scrap. Available high manganese scrap can be usefully employed in the charge for this reason. The low temperatures at this stage will favour the removal of sulphur by the $[FeS] + [Mn] \rightleftharpoons (MnS) + [Fe]$ reaction. It is essential to keep the bath temperature down by continually pushing the scrap away from the door and drawing it off the banks. This will aid low temperature reactions and preserve the furnace refractories. Fracture samples are taken to give some indication of the carbon content of the bath. When the metal is hot enough to take it, ore is fed in sufficient quantity accompanied by lime to prevent the formation of the thin, oxidising slag which attacks the banks and removes neither sulphur nor phosphorus.

Limestone is not used at this stage, as it would give rise to a frothy slag instead of the open boil necessary for inclusion removal. As the scrap is pulled off the banks and the bath picks up heat, the power input is reduced without dropping the voltage too low. This would cause a short arc, and the ends of the electrodes would dip into the slag and react with it, resulting in a frothy slag and wastage of electrode. A long arc giving a hot fluid slag and an open boil is preferable.[25] The furnace door should be left open to prevent pressure build-up, which would lower the rate of carbon removal according to the expression :—

Velocity of carbon removal $= K_1C. FeO - K_2.pCO.$

If a strongly basic slag is maintained, thinned if necessary with spar, the violence of the boil, aided by the high temperature, will eliminate a considerable proportion of the sulphur in spite of the high concentration of iron oxide in the slag. The high lime content of the slag coupled with the heavy concentration of iron oxide, will overcome the adverse thermal conditions and enable phosphorus removal to continue right up to the end of the oxidation period.

By the time the bath is clear-melted, the carbon should be below $0 \cdot 15\%$. A small feed of ore will suffice to bring it down to the required figure, which will depend on the type of steel being made and other factors. The addition of $0 \cdot 10\%$ manganese after the boil has subsided will increase the MnO in the metal ready for deoxidation by ferro-silicon after slagging-off 10 mins. later. It would probably be better to melt out at $0 \cdot 15$–$0 \cdot 25\%$ carbon and boil down, but the economic disadvantages would outweigh the benefits.

The use of the hot metal process[33] would enable a boil of sufficient intensity and duration to be maintained on each heat with consequent production of standardised conditions, better steel, and lower costs.

33 Dufty. *British Steelmaker*. May. 1941.

Electrolytic Manganese Alloyed with Copper and Nickel

For radio work, and sometimes in other connections, it is desirable to pack as much electrical resistance in as small a space as possible ; for this purpose a group of extraordinarily high-resistance alloys is discussed, resulting from an investigation of the effect of electrolytic manganese on the properties of Mn-Ni-Cu alloys.

IN radio work and in some other connections it is desirable to pack as much electrical resistance into as small a space as possible. Early investigations on the manganese-copper system and on the copper-nickel-manganese system of alloys have shown the presence of alloys with high electrical resistance in the manganese rich regions of these systems. Such alloys, however, made with silico-thermic or alumino-thermic manganese, were very brittle, and it is only within recent years that investigations on electrolytic manganese, reported workable manganese-copper and manganese-nickel alloys with resistivities approaching 200 microhm–cms., among the highest ever recorded for ductile alloys. A further investigation has just been carried out by B. L. Averbach* to determine the effect of electrolytic manganese on the properties of the ternary copper-nickel-manganese alloys.

This investigation has shown the entire copper-nickel-manganese system to be ductile with the exception of alloys containing over 97% manganese and certain binary manganese-nickel alloys, containing 50% to 75% manganese. An alloy containing 80% manganese and 20% nickel was ductile, an alloy containing 90% manganese and 10% nickel was brittle, while an alloy containing 95%

manganese and 5% nickel was again ductile. At the 50 : 50, Mn : Ni ratio, 2% of copper was sufficient to stabilise the ductile gamma phase after a drastic quench from 950° C., but at the higher manganese ratios only 1% of copper was necessary to insure cold malleability, and as more copper was added the less drastic was the quench to retain the gamma modification. An alloy containing 97% manganese, 1% nickel, 2% copper was ductile as cast, but became brittle upon slow cooling because of the precipitation of the beta phase, and a drastic quench from 1100° C. was necessary to restore the ductile gamma form. An alloy containing 96% manganese and 4% copper behaved in a similar manner, while an alloy containing 97% manganese, 2% nickel, 1% copper was extremely brittle and glass hard, and no treatment could make it workable.

Electrical resistivity determinations made on manganese-nickel-copper alloys as cast, as cast and quenched, and after a 98% reduction showed that there was a large area between 40% and 80% manganese in which high resistivity materials occurred and that the resistivity depended largely upon the manganese content. The substitution of nickel for copper had little effect upon the resistivity of the alloys. With 67% manganese cold work, solid solution

and ageing treatments had little effect on the resistivity or the ductility of those ternary alloys. A 2 : 1 ratio of Mn : Cu provided a series of alloys with the resistivity just under 200 microhm-cms., which showed a slightly decreasing resistivity as nickel was added, and little change after thermal treatment and cold work. When the Mn : Ni ratio was 50 : 50 the electrical properties exhibited large fluctuations upon treatment, and such alloys suffered a loss in ductility as well as a loss in resistivity on ageing, and this effect was noticeable for alloys containing as much as 25% copper. After ageing, an alloy containing 97% manganese, 1% nickel and 2% copper, and an alloy containing 96% manganese, 4% copper had their resistivity increased from 100 to 200 microhm-cms., but both alloys became extremely brittle.

Most of the tenary alloys at 67% manganese had a low coefficient of resistance, the order of magnitude being $+ 0\cdot5 \times 10^{-4}$ per deg. C. with the coefficients usually positive when copper was in excess of nickel. An alloy containing 60% manganese, 39% nickel, 1% copper had a coefficient of zero up to 75° C., while at the 50 : 50 ratio of Mn : Ni and at the 2 : 1 ratio of Mn : Cu the coefficients were of the order of $+ 0\cdot9$ to $-1\cdot7 \times 10^{-4}$ per deg. C. The lowest negative coefficient obtained in the investigation, $-8\cdot4 \times 10^{-4}$ per deg. C. was obtained for an alloy containing 63·4% manganese, 5% nickel, 31·6% copper. Alloys with 75% manganese showed considerable variation in coefficients, while 80% manganese alloys had low coefficients except where the copper was high in relation to the nickel. Both the manganese-copper and the manganese-nickel binary systems showed high coefficients, and at 95% manganese, 5% copper the highest positive coefficient was observed at 20×10^{-4} per deg. C.

None of the alloy investigated developed a high thermo-electric force against copper, and, in general, with the ternary alloys, the greater the copper content the more negative was the thermoelectric force. An alloy containing 67% manganese, 28% nickel, 5% copper and an alloy containing 67% manganese, 22% nickel, 11% copper had particularly low values developing up to $-0\cdot15$ micro-volts per deg. C. An alloy containing 60% manganese, 30% nickel, 10% copper had practically no e.m.f. up to 75° C. Neither the 50 : 50 Mn : Ni nor the 2 : 1 Mn : Cu series produced alloys of particularly low thermal e.m.f., while the 75% to 90% manganese alloys showed thermoelectric forces which were generally negative. Both the manganese-copper and the manganese-nickel binary alloys developed negative thermoelectric forces, and while in the manganese-copper system the e.m.f. became less negative as the copper content increased, neither system developed as low a thermoelectric force as the corresponding ternary alloys.

In order to ascertain whether silver was more effective than copper in stabilising the ductile modification of manganese, up to 5% of silver was added to the 50 : 50, Mn : Ni series of alloys. The resistances of such alloys were high as-cast, but no heat-treatment made such alloys ductile. An alloy containing 67% manganese, 32% nickel, 1% silver did produce a ductile alloy, and this alloy had a zero temperature coefficient up to 75° C. In those alloys, silver and copper were roughly equivalent, but the silver-bearing alloys tended to form porous castings.

X-ray investigations on an alloy containing 49% manganese, 49% nickel, 2% copper after it had been quenched from 950° C. showed a face centred cubic structure with a lattice parameter of 3·651A. This alloy was ductile and had a resistivity of 204 microhm-cms., and on ageing at 500° C. it became extremely brittle and the resistivity dropped to 152 microhm-cms. X-ray examination after ageing showed the presence of definite superstructure lines, and indicated that, in addition to changing to the tetragonal lattice, the atoms had so arranged themselves that the structure could be represented by two intersecting base-centred tetragonal lattices of manganese and nickel atoms. When the crystals axes were rotated 45 degs., this structure further simplified into two interlocking simple tetragonal lattices of manganese and nickel, and this ordering of the lattice appeared to account for the drop in resistivity and also for the brittleness because of the presence of separate planes of manganese and nickel. Metallographic examination showed that in addition to the change in structure, ageing had brought about the precipitation of a new phase at the grain boundaries, and that such a precipitate could in itself cause brittleness and would also tend to lower the resistivity.

In the manganese-copper system previous investigations have shown that ageing at 500° C. produced a drop in resistivity, for alloys with less than 90% manganese, without an accompanying embrittlement. X-ray examination of an alloy containing 67% manganese, 33% copper showed that before, as well as after ageing at 500° C., the structure was face-centred cubic with no evidence of super-lattic lines in either case. After ageing, however, the lattice shrank from 3·743A to 3·719A or 0·64%, while the resistivity decreased from 184 to 126 michrohm-cms. or 37·5%. Metallographic examination of the aged alloy showed no evidence of precipitation, so that for this alloy the decrease in resistivity cannot be attributed to the formation of an order lattice or to the precipitation of another phase, but it may be attributed to the contraction of the lattice.

Two alloys in the series investigated were of particular note, one containing 67% manganese, 28% nickel and 5% copper, and the other 60% manganese, 39% nickel and 1% copper. Both have an electrical resistivity of 220 michrohm-cms., more than four times the resistivity of manganin, along with a temperature coefficient and a thermoelectric force against copper which compare favourably with manganin. In the thermal treatment of the manganese-nickel-copper alloys extreme care was necessary to prevent excessive scaling and loss of manganese from the surface, a protective atmosphere being required at 300° C. At 800° C. a low-manganese case was formed in a few moments.

Liquid Helium

An interesting development in the world of science during recent years is the discovery of the high fluidity of helium by Professor P. L. Kapitsa, Director of the Institute of Physical Problems. Helium is a gas that liquifies at a lower temperature than any other known gas. This temperature, just a few degrees above absolute zero, is one at which all remaining gases are solid. Kapitsa succeeded in showing experimentally that, at extremely low temperatures, liquid helium possesses an insignificant viscosity. In his experiments the size of the opening through which liquid helium took one second to flow was so small that he computed a similar amount of water at the same pressure would take thousands of years to trickle through ; for this reason he called this phenomenon observed in liquid helium suprafluidity.

Earlier data indicated that liquid helium possessed tremendous thermal conductivity ; as a result of his work, however, Kapitsa was able to show that in reality the thermal conductivity of liquid helium is not great, certainly not unusual, and that the seemingly large thermal conductivity is definitely connected with the suprafluidity of the liquid.

When he undertook his research on the behaviour of liquid helium, Kapitsa found he needed larger quantities of the gas than were available to him with the plant at his disposal. In a comparatively short time he developed a new type of liquid helium machine operating on entirely different principles. This new machine produces approximately one gallon of the liquid per hour, and large quantities have been placed at the disposal of scientists in the Soviet Union.

Scientific and Technical Institutes in War-Time

THE amount of time, thought and money applied to the solution of engineering problems and to development in the various fields it represents is impressive in normal peace-time activities. That there is ample need for the adoption of this policy is generally appreciated. It is recognised that it is only possible to maintain a progressive position by retaining the initiative resulting from the steady and persistent study of the many problems that continually arise. Discoveries in the metallurgical field, upon which much engineering progress depends, are relatively few, and, when they do happen, they are generally the prelude to much research before they can be profitably applied. As a rule, the field is so vast that the work of weeks and even months is necessary to obtain a right conception on one minor detail in the theory evolved with the object of applying it in practice. Progress is largely achieved, however, by developments.

Fundamentally, the position remains unchanged in times of war, but much of the study is directed to the war machine, and pressure upon the various scientific and technical services becomes more acute, since to prosecute the war successfully the nations engaged must retain the initiative in the character and quality of the machines placed at the disposal of its fighting forces. War, in fact, sharpens the need for exploring every avenue likely to improve the fighting capacity of the nation. There is ample evidence that the results of research are contributing in an increasing extent to Britain's war effort, but there is still much waste of scientific ability through lack of adequate co-operation between firms engaged on similar Government contracts. Frequently production is held up in one factory while its technical staff overcome difficulties already surmounted by parallel organisations engaged on similar work.

In this country the majority of large works are now equipped with laboratories adequately equipped for dealing with the routine work of analysing and testing, and for investigating operating plant and manufacturing problems, but only in exceptional instances is there time for prolonged research. In many cases the problems are of such magnitude in their effect on an industry that the necessary scientific work involved cannot be satisfactorily carried out by an industry unaided. Under such conditions the State has an interest in assisting the solution of problems affecting industry and in fostering the development of the results of research. This is the main purpose of the Department of Scientific and Industrial Research, which is active in mobilising available scientific forces in support of industry. Much of this work is done through committees appointed by the Department. A considerable amount of valuable research work is carried out at the National Physical Laboratory, at the Woolwich Research Department, and a number of other laboratories operating under the direction of the Department of Scientific and Industrial Research. The universities and technical colleges also contribute valuable work, while many research associations, like the British Non-Ferrous Metals and the British Cast Iron Research Associations, in addition to activity in their scientific work, give much attention to the practical application of the results of research in their particular field.

Each of the various industries, however, has its own organisation which provides a means of communication to its members on matters bearing upon their respective interests, arrange meetings to discuss practical and scientific problems relating to manufactures within the scope of each, and generally providing facilities for the advancement of both practical and scientific knowledge. Thus, the Iron and Steel Institute, the Institute of Metals and the Institute of British Foundrymen are representative examples of these individual Associations which are doing excellent work in increasing knowledge among its members. The war has presented fresh problems to the Councils of these Associations, but their value to members faced with special technical problems in their daily work has been intensified, and it can be said that these Associations are functioning at least as actively and helpfully in the interests of this country and its allies as they did in the war of 1914-18, when various Government Departments made extensive use of facilities rendered available by the Institutes.

The normal activities of these institutes have been curtailed, but those activities useful in the successful prosecution of the war are being maintained. Research committees are very busy, but most of their attention is directed to war-time problems ; long-range research is only being maintained where it does not impede work of immediate practical importance, or where interruption would result in undue waste of past effort, or where the results are considered to be of value to the country in the post-war reconstruction. A good deal of the research work, especially that directed to matters of immediate importance, is confidential, and results cannot be published until after the war, but they are applied in industry as quickly as possible when they are proved to advance production or improve products necessary to the war effort.

Local meetings of institutes and societies continue to be held throughout the country ; some sections have even been more active than in peace time, arranging meetings throughout summer months as well as in winter, and these meetings have been remarkably well attended and have resulted in good and helpful discussions. In some cases joint meetings have been organised with a number of local societies in order to provide opportunities for technical discussion. In addition to meetings, however, some institutes, such as the Institute of Metals, have created an information and advice service which has proved invaluable to many members. These institutes are in close touch with the Services and Government Departments, and give assistance in various directions. For instance, the Iron and Steel Institute is in close touch with the various Controls of the Ministry of Supply, especially the Iron and Steel Control, the Chrome Ore, Magnesite and Wolfram Control, and the Foundry Bonding Materials Control ; the appropriate research committees co-operate with them, assisting industry to adopt practice to wartime conditions, and advising the authorities on the technical effects of measures proposed by them.

Although the technical institutes are undoubtedly making a useful contribution to the war effort, there is room for a greater effort. There is much criticism of wasted time in solving problems in some works that have been solved previously in other works. A need exists for centralised co-ordination of technical and scientific research and development and for real pooling of information and facilities, between Government Departments, between manufacturers, and between Government Departments and manufacturers,

British Merchant Shipping

IN our last issue we discussed production for the war machine, and endeavoured to emphasise that the adjustment of the industrial organisation of this country to meet the various demands of our Fighting Forces has been no light task. Much has been done in this direction, and much still remains to be done before production will satisfy the needs for the successful prosecution of the war. There is one aspect of production, however, which is not less vital than production for the war machine and that concerns our Merchant Shipping. The never-ceasing struggle to bring materials of war and food supplies to these shores, and to maintain contact with our Forces overseas, against the persistent efforts of U-boats, surface raiders and long-range bombers, has resulted in constant and inevitable losses.

Until the spring of the present year it had been possible to confine average monthly losses to a rate of approximately five million tons per annum, and there was considerable hope that Britain would be able to carry on until effective replacements became available. British, Allied and neutral shipping losses in the spring, however, rose sharply to an annual rate approaching six million tons. Sinkings for March, April and May were 489,000, 488,000 and 461,000 tons respectively, and this rapid widening of the margin between sinkings and potential replacements brought the shipping situation to a critical stage. Lower losses were experienced in June when the tonnage affected amounted to 329,000 tons. These were the last figures announced by the Admiralty, but statements have been made by reliable authorities which indicate a more satisfactory trend. Mr. A. V. Alexander, for instance, has said that shipping losses in July had been " easily the best " for the 15 months since he became First Lord of the Admiralty. He also remarked that in August the figures have been equally good.

The possession by the Germans of strategic bases on the two thousand mile coast line from Narvik to Bayonne has enabled them to launch vicious assaults on all merchant shipping approaching the British Isles, and in the summer and autumn of 1940 losses were particularly heavy.

The lower losses in recent months probably reflect Germany's present pre-occupation with Russia and should not at this time be used as a basis for future estimates. Provided that losses do not get out of control and every remaining source of tonnage is utilised to the fullest extent, British authorities are confident that it will be possible to carry on through what may be the coming critical months without serious impairment of the war effort. As pointed out, however, in the recent *Monthly Letter* of the Royal Bank of Canada, such measures cannot in themselves be relied upon to shift the balance of offensive power from Germany to Britain. The only real answer to the problem —which must involve large additional amounts of aid from the United States to Britain—is new ship construction.

At the outset of the present war Britain owned or directly controlled a merchant marine of approximately 21 million tons. Since that time, through the capture of enemy shipping, acquisition of the merchant fleets of occupied countries, purchase and charter of neutral shipping and new construction within the British Empire, she has acquired direct control over an additional 11 million tons. Against the total of such credits must be placed admitted losses by enemy action of approximately six to seven million tons, leaving some 24 to 25 million tons of shipping still available for use. This amount, while representing a gain on that controlled at the outbreak of hostilities, cannot be considered a net increase in available tonnage, since in pre-war years a substantial proportion of Britain's commerce was carried in foreign vessels. In addition to deductions for sinkings, allowance must be made for ships that are unsuitable for freight transport ; tonnage laid up for repairs at any one time ; and the requisition of substantial tonnage for Army and Navy auxiliaries. A final allowance for shipping employed on routes far removed from the battle zone will reduce the tonnage directly supplying the British Isles to approximately 15 million tons.

Normal standards are useless in assessing the carrying power of this remaining tonnage. Under present conditions effective tonnage is related not so much to the number of ships available but to the number of round trips that can be made in a given period between British ports and the countries with which Britain is trading. Despite the blockade of Europe, resulting in the release of large quantities of shipping for other purposes, the establishment of import controls and the more economical operation of all vessels, British shipping is handicapped in many directions. Convoys proceed at the speed of the slowest ship, journeys are longer due to the elimination of Europe as a source of supply and the dangers of the Mediterranean, and delays in ports due to congestion are almost unavoidable ; these factors greatly impair the effectiveness of the merchant service.

It must be remembered that the rate of sinkings, especially in the spring of this year, was far in excess of British shipyards to replace them. Most estimates of merchant shipping construction in the British Isles during the current year are in the neighbourhood of one million tons. It is probable that this is a very conservative estimate, but it will be appreciated that Naval building and the constant repair of damaged vessels have reduced the ability of shipyards to handle other work ; added to this is the shortage of skilled labour. Another factor which has proved a handicap is the rationalisation plan put into operation in pre-war days when there was less demand for ships. Large orders have been placed in Canada, Australia, New Zealand and South Africa, but the benefit of this new construction will not be realised for about twelve months. In most instances an initial expansion in shipyard capacity was necessary. Most of the effort of the British Dominions to date has been devoted to the construction of small naval vessels designed to counter the submarine menace.

Every effort should be made to swell the total of ship construction from every source, but the United States is the only country with the resources necessary to furnish a satisfactory solution to this shipping problem. If the United States could repeat the construction of the enormous tonnage she produced in 1918, the contribution would be invaluable. Unfortunately, conditions have changed since that time, and construction of merchant ships in that country during this year is not likely to exceed one million tons. Recently, however, Mr. Harry L. Hopkins announced that United States shipyards will complete and make ready for sea at least six million tons of merchant shipping during 1942.

The present trends indicate that the shipping situation is less serious than it was in the spring, and that, providing average losses do not greatly increase, it can be met by stringent economies in the use of tonnage, by the mobilisation of all existing shipping resources beyond German control, by means of more adequate protective measures, by increasing the production capacity of shipyards in Britain and the British Dominions, and by increased facilities afforded by the United States. With the rapid strides already made there is real prospect that by the end of 1942 the tide will have turned and that replacements will more than take care of losses.

A Simple Gas-testing Appliance

THE short article by Mr. J. G. Lewis, published in our August issue under the above title, was extracted from the current issue of the " Wild-Barfield Heat-Treatment Journal," by kind permission of Messrs. Wild-Barfield Electric Furnaces Ltd.

Intergranular Corrosion in Austenitic Stainless Steels—Part III.

By J. H. G. Monypenny, F.Inst.P.

The occurrence of intergranular corrosion in austenitic chromium-nickel steels, its detection, cause and prevention and the effects it produces, are discussed. In the practical application of these steels this trouble has been largely overcome, though not entirely, and in this article the author takes stock of the present position, studies in some detail the effect of different variables, and points out where satisfactory results can be obtained in the industrial use of the steels and where further improvements are still desirable. Attention is given mainly to the 18-8 steels, as these are the most widely used of the austenitic stainless steels, but the author emphasises that intergranular corrosion is not confined to steels of this composition.

HAVING described the underlying causes of intergranular corrosion and the mechanism of its production, one may next consider methods for preventing its occurrence. Several methods are possible :—

(a) Reduction of carbon content so that no carbide is precipitated during heating at any temperature.

(b) Control of carbide precipitation so that continuous films of chromium-depleted material are not produced ; this may be achieved in the plain chromium-nickel steels, or it may be aided by the presence of other alloys.

(c) Addition of suitable alloys which will either cause the precipitation of carbides other than that of chromium or will increase the solubility of carbon in the austenitic matrix.

No alloy has yet been found which will increase appreciably the solubility of carbon in the austenitic matrix. All the other methods, however, have been used with varying degrees of success.

On the basis of the theory expounded in the first part of this article, carbon content is the primary cause of intergranular corrosion, and results which have been obtained show that the intensity of intergranular attack increases broadly with carbon content. Thus Fig. 11 gives results by Bain, Aborn and Rutherford,[25] showing the relation between carbon content and the maximum rate of attack obtained on heating various steels for 1,000 hours at temperatures within the sensitising range. Apart from the fact that the diagram shows this relation to be very close, it is also interesting from two other aspects. It indicates that complete freedom from attack may be expected with a carbon content not exceeding 0·02%—an almost impossibly low figure in the commercial production of steel at present, though claims were made two or three years ago that values of this order could be obtained in practice—and also that with carbon contents commonly regarded as low—e.g., 0·06% or thereabouts—very marked intergranular susceptibility may be produced by prolonged heating at suitable temperatures. Practical interest in these low-carbon steels, however, is not generally concerned with their behaviour after such treatment conditions, but rather with their relative freedom from attack when heated in the sensitizing range for such short periods as may occur in welding or other fabrication processes, and here the question of their maximum " safe periods " becomes of paramount importance. From this aspect, the effect of carbon content does not appear to be so definite and clear cut as it is with maximum rate of attack ; thus practical experience in the testing of numbers of low-carbon casts indicates that their " safe periods "—e.g., at 650° C.—are not always directly related to the reciprocals of their carbon contents. While this may be due partly to the effects of variation in grain size—undissolved carbide is hardly likely to be a marked feature of steels containing less than 0·1% carbon after

softening at 1,100° C.—and to the fact that there are limits to the accuracy with which such small amounts of carbon can be determined, it inevitably raises the question as to whether other elements could function in a similar manner to carbon in forming compounds, with chromium, whose solubility in austenite increases with temperature. Nitrogen is a possibility in this respect, as it forms a well defined nitride with chromium and it is known from Adcock's investigations[26] to function from a structural point of view in a similar manner to carbon in iron-chromium alloys. Should nitrogen act similarly to carbon as regards intergranular susceptibility, it would probably be less effective because the nitride contains a lower percentage of chromium than the carbide. The fact, however, that discrepancies
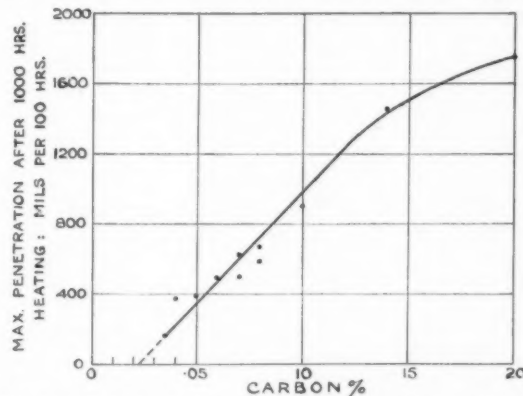

Fig. 11.—Relation between carbon content and maximum susceptibility of " 18-8 " steels (Bain, Aborn and Rutherford).

exist between the behaviour of low-carbon steels during short periods of heating at 650° C. and their carbon contents as determined in the usual manner, makes it advisable to test each particular cast—by determining the maximum period it can be heated (e.g., at 650° C.) without developing a detectable amount of susceptibility—rather than to assume that its behaviour when so heated can be predicted from its ascertained carbon content. Such tests should of course be carried out on samples which have previously been adequately softened in a standardised manner. Most " low-carbon steels " on the market contain less than 0·1% carbon, but rarely is the value below 0·06%. Tests on a number of such steels—both of British and foreign manufacture—have shown that their " safe periods " at 650° C. may vary from 1 min. to 30 mins. or even more. Those in the former category have a very restricted sphere of usefulness in welding operations, whereas those free from susceptibility after heating for 30 mins. would be suitable for most welded constructions. This wide variation in properties emphasises the necessity for carefully testing each steel in the manner recommended above.

25 " The Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels." E. C. Bain, R. H. Aborn, and J. J. B. Rutherford, *Trans. Am. Soc. Steel Treat.*, XXI (1933), p. 481.

26 " The Effect of Nitrogen on Chromium and Some Iron-Chromium Alloys," F. Adcock. *J. Iron and Steel Inst.*, 1926, II, p. 117.

Control of carbide precipitation so as to prevent the production of continuous membranes of material impoverished in chromium is made possible, in steels to which no other special alloy has been added, by the fact that the rate of chromium diffusion increases rapidly with temperature above about 800° C., whereas the limiting solubility of carbon does not increase markedly below 900°–950° C. Hence, if a steel be heated for a sufficient time at, for example, 900° C., carbon in excess of 0·06%,* remains precipitated as chromium carbide, but, as a result of chromium diffusion, the carbide particles are embedded in austenite of reasonably uniform composition and are no longer sandwiched between layers depleted in chromium. Steel so treated behaves, when subsequently heated at 650° C. or thereabouts, as though it contained only 0·06% carbon, provided, of course, it has not been reheated in the meantime to any temperature above 900° C. Lowering this stabilising temperature to 850° C. reduces the carbon remaining in solution to a still lower figure—about 0·04%—but increases considerably the time required to bring about adequate diffusion.

Such a stabilising process may be carried out comparatively easily in laboratory tests on small pieces of strip or sheet, which may be heated rapidly to 850° or 900° C., but, as already mentioned, a considerable amount of intergranular carbide would be precipitated during the much slower heating necessary for large articles or complex pieces of plant, and this would necessitate a long period of heating at 900° C.—probably 24 hours or more—in order to remove completely the intense chromium depletion from the grain boundary layers adjacent to the carbide. For this reason the method, though possible, is frequently hardly practicable, and the difficulty of its application increases with the carbon content of the steel. It is interesting to note, however, that it has been applied successfully to forms of chemical plant—e.g., tubular heat exchangers—which were required to work continuously at 500°–600° C. or thereabouts, in contact with corrosive gases. The tubes and end-plates of these heat exchangers were made of " 18–8 " steel, containing about 0·08% carbon, and, after welding was completed, the tubular unit was thoroughly annealed at 850° C. so as to precipitate as much carbide as possible in an innocuous form. The heat exchangers have since given satisfactory service over a period of several years.

The time necessary to obtain adequate diffusion of chromium can be reduced considerably by prior cold work. When cold-worked austenitic steels are reheated, carbide is precipitated not only at the grain boundaries, but also on all the slip planes on which movement has taken place during deformation, as is shown in Fig. 12.† The area on which precipitation occurs being thus increased so enormously, the density of precipitation is correspondingly reduced, and with it the degree of chromium impoverishment in the adjacent austenite. Hence susceptibility, although it develops quickly in cold-worked material—rather more quickly, in fact, than in material of the same composition fully softened—does not reach so great an intensity on further heating, and is much more rapidly removed by diffusion of chromium. Thus, Rollason[27] showed that steel containing 0·17% carbon, when heated at 650° C. after being softened at 1,150° C., became more and more susceptible as the period of heating increased to about 300 hours and with still longer periods showed gradual recovery. The same steel after being reduced 75% by cold-rolling reached maximum susceptibility after heating for 4 mins. at 650° C. and recovered complete resistance to intergranular attack after heating for an hour at that temperature. Bain, Aborn and Rutherford[25] found a similar effect in steel containing 0·08% carbon, which they tested as softened, and after 50% reduction in thickness by cold-rolling. Samples in each condition were

* See curve A, Fig. 1, in the first part of this article; this journal, July, 1941, p. 78.
† The author is indebted to Dr. Aborn for this extremely good photomicrograph.
27 " Some Effects of Cold Rolling on the Intergranular Corrosion of the 18–8 Stainless Steels," E. C. Rollason. *J. Iron and Steel Inst.*, 1931, I, p. 311.

heated for 1 hour and for 1,000 hours at temperatures, rising by steps of 10°–20° C., between 200° and 800° C. The results they obtained are summarised in the following table, the rates of penetration being measured by the electrical resistance method.

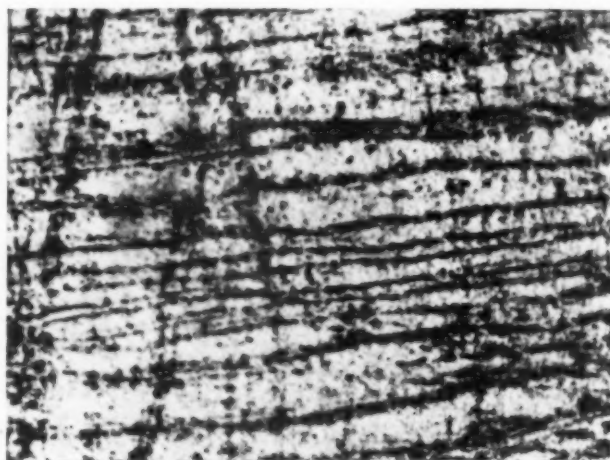| —	Period of Heating.	Softened Steel.	Steel Reduced 50%, by Cold Rolling.
Range of temperature producing susceptibility.	1 hour	560°–730° C.	480°–610° C.
	1,000 hours	510°–650° C.	350°–460° C.
Temperature giving maximum rate of attack.	1 hour	640°–660° C.	520° C.
	1,000 hours	540°–610° C.	410° C.
Maximum rate of attack, mils, per 100 hours.	1 hour	70	22
	1,000 hours	600	47

Fig. 12.—Carbide precipitation on slip planes of cold-rolled " 18–8 " steel. × 2000.

These various results indicate that steels containing, for example, 0·15% carbon, if cold-rolled or otherwise cold-worked to a sufficient extent and then heated—e.g., at 700°–800° C.—for an hour or two, would be completely free from intergranular susceptibility if subsequently reheated at lower temperatures; all the carbide they contained, above the solubility limit, would exist as particles embedded in an austenitic matrix of substantially uniform composition. As a practical method of dealing with intergranular corrosion, however, the process has several disadvantages:—

(1) Reheating to 700°–800° C. softens cold-worked austenitic steels only partially; thus strip or sheet cold-rolled 50% and softened in this temperature range would have a Brinell hardness number of 250–300, and hence would be unsuitable for many fabrication processes.

(2) Material which has been stabilised in this way must not be heated to higher temperatures or it will lose wholly or partially its special properties. Not only does this preclude subsequent hot-working operations or softening treatments at temperatures about 800° C., but it means that susceptible material will be produced where two or more welds cross or meet. During the first welding operation material adjacent to the weld is raised to high temperatures, some or all of the precipitated carbide being thereby taken into solution; the carbide so dissolved will be reprecipitated in intergranular form in any place which is heated to a dull red heat in a subsequent welding operation.

(3) Although the intense chromium depletion in the layers adjoining the precipitated carbide—the direct cause of intergranular attack—has been removed by diffusion, the formation of the carbide has reduced the chromium content of the matrix to an appreciable amount; about 1·5 or 2%, if the total carbon content

be 0·15%. The matrix is thus less resistant to general corrosion than when fully softened.

(4) The process can only be applied to material in a form—e.g., strip or sheet or wire—which readily allows heavy cold-working.

The disadvantages of incomplete softening can be reduced by using a rather higher reheating temperature—e.g., 900° C. or perhaps 950° C.,—but in so doing some carbide is taken into solution and hence the immunity from intergranular susceptibility on subsequent reheating at 650° C. or thereabouts is partly lost.

It may be noted that " cold-working " implies working below the temperature at which recrystallisation occurs during the working process, and, in the case of the austenitic steels, this temperature is probably about 850° C. The final hot-rolling of sheets can be carried out from an initial temperature of this order, or certainly of not higher than 950° C. Precipitation of carbide will, of course, occur during such " hot " rolling operations, but while the latter are below the recrystallisation temperature, the carbide will separate out on the slip-planes as well as at the grain boundaries. The actual rolling will also tend to make the precipitated carbide ball up more quickly, so that sheets so rolled will rapidly become free from chromium depletion when subsequently reheated at 950° C. or thereabouts. Treatment at the latter temperature would not fully soften the sheets, but probably their Brinell value would not

Fig. 13.—Minimum amounts of titanium required to give freedom from intergranular corrosion in " 18–8 " steels of various carbon contents.
Curve A—Houdremont nad Schafmeister. (29)
   ,,   B—Bain, Aborn and Rutherford. (25)

greatly exceed 200 ; it could be reduced further by raising slightly the heat-treatment temperature with, of course, a corresponding loss in the efficiency of the elimination of intergranular susceptibility.

By careful control of rolling and subsequent heat-treatment temperatures, sheets and thin plates have been produced in Germany, from steel containing 0·12–0·15% carbon or thereabouts, which can be fabricated with reasonable ease and are suitable for single-run arc welding—without subsequent heat-treatment—provided they are subjected in use to mildly corrosive conditions only. For example, material so prepared has been used in Germany and other European countries for the manufacture of equipment for the dairy and brewing industries. One presumes it has been so used, in spite of its limitations, because it is somewhat cheaper than sheet in which freedom from intergranular corrosion has been obtained by other more satisfactory means.

Raising the nickel content of " 18–8 " steel to 15% or so lowers substantially the temperature required for adequate softening, as has been shown, for example, by Pfeil and Jones.[28] Such material, after heavy cold-rolling, followed

by softening at about 850° C., would probably be soft enough for ordinary fabrication processes, and, at the same time, would be reasonably free from intergranular susceptibility. The cost of the extra nickel is considerable, however, and as the material would still be subject to the restriction that it must not be hot-worked or softened at higher temperatures than 850° C. by the fabricator or it would lose its special feature more or less completely, and, in addition, it would be liable to intergranular weakness at crossed welds as described above, there seems little likelihood of such material being used in practice.

Most of the austenitic stainless steels, produced commercially, which do not suffer from intergranular corrosion, owe their properties in this respect to the presence of certain special alloying metals. Those whose addition has been suggested for this purpose include columbium, molybdenum, silicon, tantalum and other " rare earth " metals, titanium, tungsten and vanadium. All these metals possess two features in common ; they form stable carbides, and when added in sufficient amount to carbonless iron they prevent the formation of gamma iron. Both these features are of value in combating intergranular corrosion.

The precipitation of a carbide other than that of chromium would obviously prevent the formation of the grain boundary layers, largely depleted of chromium, which are the immediate cause of intergranular corrosion. For this purpose, it is not on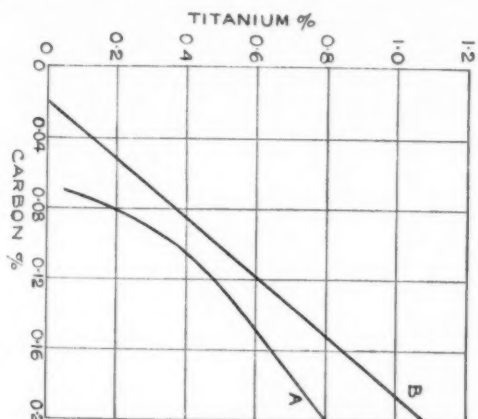ly necessary that the added metal should form a stable carbide, but that the latter should be less soluble than chromium carbide in the austenitic matrix. This feature appears to be characteristic of the carbides of tantalum, titanium and columbium, but to be less marked with the carbides of the other metals mentioned above ; the latter
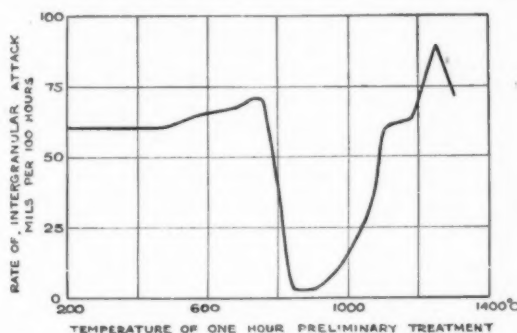

Fig. 14.—Rate of intergranular attack of titanium-treated " 18–8 " steel as affected by a preliminary heating of 1 hour at various temperatures. Treatment to induce sensitization was 100 hours at 600° C. (Bain, Aborn and Rutherford). (25)

metals seem to reduce intergranular susceptibility mainly by reason of their power to produce a duplex structure of austenite and ferrite instead of one purely austenitic.

Houdremont and Schafmeister[29] investigated the effects of titanium additions, and as a result of tests on a large number of steels, concluded that, for a given carbon content, the amount of titanium in the steel should not be less than is indicated by curve A in Fig. 13 in order to remove intergranular susceptibility ; they mention that in general this means a titanium : carbon ration of 4 : 1, corresponding to that in the formula TiC. They state that such additions are effective not only for short periods of heating in the critical temperature range—such as occur in welding operations,—but also for much longer periods ; thus heating for up to 1,000 hours at 500°–800° C. is stated to have had no injurious effects on the titanium-treated steels. From their own results, described in the next paragraph, it is obvious, however, that this claim for complete freedom can only be true if the steel has been heat-treated in a particular way, a fact confirmed by other investigators—e.g., Bain, Aborn and Rutherford.[25]

Houdremont and Schafmeister considered that the beneficial effect of titanium arose from the fact that at forging and rolling temperatures the carbon in the steel existed mainly as particles of titanium carbide and hence

28 " A Contribution to the Study of the Properties of Austenitic Steels." L. B. Pfeil and D. G. Jones. J. Iron and Steel Inst., 1933, I., p. 337.

29 " Prevention of Intergranular Corrosion in Steels containing 18% Cr and 8% Ni." E. Houdremont and P. Schafmeister. Archiv. f.d. Eisenhuttenw., vol. VII, p. 187 (September, 1933).

could not precipitate in a dangerous form when the steel was subsequently heated at lower temperatures. As evidence of this action, they determined the amounts of titanium existing respectively as carbide and dissolved in the austenite in samples of steel containing 0·14% carbon, 18% chromium, 9·04% nickel, and 0·47% titanium which had been heated to and quenched from 1,000° and 1,350° C. respectively. The method of separation which they used consisted in dissolving the steel in 1 : 1 hydrochloric acid. In the sample heat-treated at 1,000° C., 0·42% TiC was present as a residue, 0·12% Ti, and 0·06% carbon being dissolved in the austenite. For the other sample heat-treated at 1,350° C., the figures were 0·16% TiC, 0·32% Ti, and 0·11% C. It will be noted that the figures for carbon solubility are well below the values given by the same authors and by Bain and Aborn[30] for carbon solubility in a plain " 18–8 " steel (see Fig. 1 in Part I of this article). In addition, Houdremont and Schafmeister pointed out that as a result of the major amount of the carbon being dissolved in the austenite in the sample heat-treated at 1,350° C., carbide is precipitated in finely divided form at the grain boundaries when this sample is subsequently heated at 650° C., thereby making the steel susceptible to intergranular corrosion. Presumably, they refer here to the precipitation of chromium carbide, a point to which reference will be made later.

Detailed information regarding the effect of titanium was also given by Bain, Aborn and Rutherford.[25] They agree with the German investigators that the titanium additions reduce the solubility of carbon appreciably—a diagram given in their paper gives the extraordinarily low values of 0·03% at 1,000° C., and 0·05% at 1,200° C. as the limiting solubility in the presence of 0·5% titanium— but stipulate a higher content of this metal as being necessary to ensure freedom from intergranular susceptibility. Their minimum requirement, indicated by curve B in Fig. 13, is six times the carbon content in excess of 0·02%, the latter figure representing the amount soluble in the austenite at 600° C. or thereabouts.

The American investigators also state that to obtain complete immunity steels containing this minimum amount of titanium should be given a stabilising treatment of 2–4 hours at 850°–900° C., basing their opinion on test results, such as those detailed in Fig. 14, where the rates of intergranular penetration are plotted of samples of a titanium-containing steel which had been heated for 1 hour at various temperatures between 200° and 1,200° C. and subsequently reheated for 100 hours at 600° C. Presumably the samples had first of all been softened in the normal manner at about 1,100° C., and one can note the efficacy of an hour's treatment at 850°–900° C. in giving complete immunity from intergranular susceptibility.

It should be noted, however, that the test used to determine whether any tendency to develop intergranular weakness existed was very drastic ; a period of heating of 100 hours at 600° C. without doubt gives valuable information regarding the behaviour of steel which is to be held more or less continuously at this temperature during use, but its indications may be quite misleading if applied to the much shorter periods likely to occur in plant fabrication processes. There is little doubt that steel containing not less than the minimum amount of titanium specified by Bain, Aborn and Rutherford, may be welded after normal softening—without any special stabilising treatment,— and will then be satisfactorily immune from intergranular attack in the neighbourhood of the welds.

At the same time, the effect of a prior stabilising treatment as indicated in Fig. 14 gives rise to some interesting questions regarding the effects of varying prior treatment on the behaviour of titanium-treated steels. At 850°–900° C. the solubility of carbon as titanium carbide is probably no greater than that of carbon as chromium carbide at 600° C. Holding the steel at 850°–900° C., therefore, allows preferential precipitation of titanium

carbide to occur to such an extent that chromium carbide cannot form during subsequent heating, even for long periods, at 600° C.—i.e., the steel so treated is completely immune from intergranular attack providing it is not subsequently heated to any temperature above 900° C. On the other hand, there is an appreciable solubility of titanium carbide at the normal softening temperature, and when such normally softened material is subsequently heated at 600° C. the carbon so dissolved will reprecipitate. Whether it will then combine entirely with titanium or partly with chromium would seem to depend on the relative availability of the atoms of these metals in the areas where they are required. If one assumes even distribution of the various elements, a representative group of a thousand atoms of an " 18–8 " steel containing 0·1% carbon and 0·5% titanium will consist of :—

Carbon, 5 atoms ; titanium, 6 atoms ; nickel, 75 atoms ; chromium, 190 atoms ; iron, etc., 724 atoms.

As Bain, Aborn and Rutherford[25] have pointed out, " each carbon atom has only to find one titanium atom for combination to form TiC, but must associate with it four chromium atoms for the building of a crystallite of Cr_4C ; but there are 190 chromium atoms for each 6 of titanium, and the purely statistical probability for forming Cr_4C as against TiC is therefore $\dfrac{190}{4}$: 6, or about 8 : 1. Hence, on the basis of availability of atoms, the urge to equilibrium (TiC versus Cr_4C) must overcome odds of 8 : 1 ; at elevated temperatures where diffusion is easy, equilibrium is reached, but at lower temperatures, where diffusion is retarded and paths of diffusion are lengthened by previous combinations, the carbon is well content to form a small amount of chromium carbide."

It may be useful, however, to examine the matter a little more closely. It seems unlikely that equilibrium will be reached in the normal softening treatment given, for example, to sheets ; heating for a couple of minutes or so at 1,050°–1,100° C. would probably dissolve only part of the carbide normally soluble at this temperature if equilibrium were reached ; the rest would remain as particles of titanium carbide. On the basis of the data given by Houdremont and Schafmeister, there might be about 0·06% of carbon in solution after such softening in steel containing 0·1% carbon and 0·5% titanium—such as is mentioned in the last paragraph,—though if the estimate given by Bain, Aborn and Rutherford[25] of the solubility of carbon in the presence of 0·5% titanium is correct, the amount would not exceed 0·04%. Assuming, however, that the German figures are substantially correct, such material when subsequently heated at 600° C. or thereabouts would precipitate carbide only very slowly and that which first formed would probably be TiC ; complete immunity would almost certainly be retained after periods of heating of 30 or 60 mins. With more prolonged heating, however, carbon diffusing to the grain boundaries from the interior of the grains might not find sufficient titanium available in the grain boundary area to form TiC, and would then precipitate as Cr_4C, thus developing slight susceptibility as shown in Fig. 14. Stabilisation at 850°–900° C. removes this slight danger by allowing preferential precipitation of TiC to such an extent as to reduce the carbon in solution to a negligible amount.

What would happen to such a steel, however, if it were heated to a sufficiently high temperature to dissolve all the carbide and obtain reasonably uniform distribution, both of carbon and titanium ? There seems no reason to assume that the mode of precipitation of titanium carbide from such a solution, at, for example, 600° C., would differ from that of chromium carbide ; i.e., it would be formed like the latter at the grain boundaries, and not in the body of the grain. One may assume, therefore, that on heating such a homogeneised steel at 600° C., the carbon in the grain boundary layers would combine preferentially with the titanium also present in these layers and form TiC,
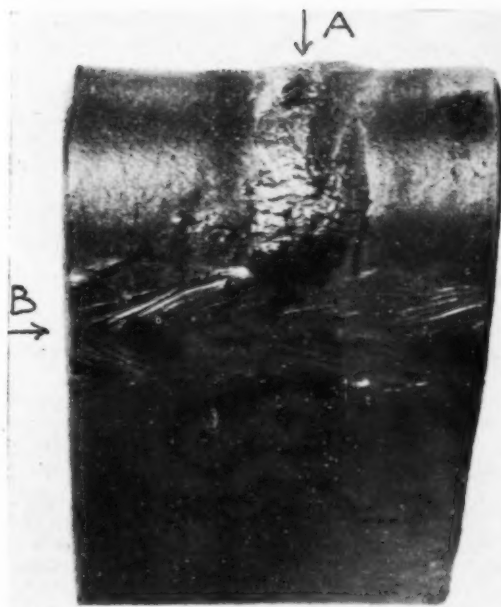
Fig. 15.—Intergranular corrosion in weld metal resulting from oxidation of titanium during welding. A—first weld; B—second weld.

but this would remove practically all the titanium existing in these layers and, unless one assumes that titanium can diffuse through the austenite as fast as carbon, and therefore very much faster than chromium—and there seems no fundamental reason why it should do—further atoms of carbon which diffused from the interior of the grains would perforce have to precipitate as chromium carbide when they arrived at the grain boundaries. It is probable, therefore, that steel heat-treated in this way would have only a relatively short " safe period " beyond which it would become appreciably susceptible even if it contained an amount of titanium normally deemed to be adequate. Houdremont and Schafmeister, as mentioned earlier, have in fact shown this to be the case with steel heat-treated at 1,350° C., and the present writer has repeatedly observed that the " safe periods " of " 18–8 " steels containing titanium are appreciably reduced by a previous softening at 1,250° C. as compared with the same steels heat-treated in the normal way at 1,050–1,100° C.

While it may be unlikely that steel would be deliberately softened at such high temperatures in ordinary heat-treatment operations, the matter is of interest in connection with welded equipment. The parent metal in the immediate vicinity of the actual fused joint (the properties of the latter will be discussed presently) is raised to a temperature approaching its melting point for a short period whose actual length depends on the speed of welding. Possibly equilibrium at this high temperature may not be reached, but it is reasonable to expect that these overheated bands will carry more carbon in solution than the normally heat-treated material, and hence—as described above—will develop intergranular susceptibility more quickly and in greater degree than the latter when subsequently heated to 600° C. or so. Probably the greater liability thus produced may not be sufficient to cause trouble if the over-heated band is heated locally by a second weld meeting or crossing it—unless the steel contained less than the normal amount of titanium,—but it would undoubtedly have an effect if, during use or for any other reason, the welded plant was subsequently heated for more prolonged periods in the sensitizing range of temperature.

The actual weld metal presents a more serious difficulty. Titanium oxidises very readily—a fact not surprising when it is remembered that it has been used for years as a final deoxidiser in steelmaking operations,—and hence when an electrode or filler rod of titanium-containing steel is melted

down, much of the titanium is oxidised. In oxy-acetylene and electric-arc welding the loss is frequently well over 60%, and even in welds made by the atomic hydrogen process a loss of 25–30% has been observed, notwithstanding the fact that there is apparently little opportunity for oxidation to occur in this process. In addition, most, if not all, of the carbon will be retained in solution in the weld metal as the latter cools rapidly from the welding heat, so that the small amount of titanium which remains in the steel is under a handicap in attempting to immunise the carbon with which it could theoretically combine. The consequence is that weld metal laid down from electrodes or filler rods of titanium-containing steel is frequently made susceptible to intergranular attack by a quite short heating at 650° C. or thereabouts ; a second weld crossing or meeting the first may be sufficient, as was the case with the weld shown in Fig. 15.

The ease with which titanium oxidises may also have a disconcerting effect in the production of numbers of small castings. A certain amount of titanium is always oxidised in the melting of steels containing this metal and normally—e.g., in the production of ingots for rolling or forging—this loss can be taken into account and a requisite amount of ferro-titanium added to cover it. The casting of large numbers of small articles, however, takes a considerable time, and while the molten steel is being transferred from ladle to shank and from shank to mould, oxidation of titanium is proceeding apace, with the result that although the castings first poured may contain the desired amount of titanium, those cast later may retain only an amount quite inadequate to give the desired freedom from intergranular susceptibility. In such circumstances there is much to be said for the use of other methods of overcoming susceptibility which do not depend on such an easily oxidisable metal as titanium.

There is one other matter concerning titanium which is of some interest and perhaps at times of some importance, its well-known capacity for combining with nitrogen. Most if not all titanium steels contain the characteristic angular inclusions which are often referred to as " cyanonitride of titanium," though one is a little curious to know what evidence there is in support of the composition which this name implies. Assuming, however, that these inclusions do in fact contain nitrogen, it may be asked how much titanium, on the average, they lock up in a form which would seem to be ineffective for the purpose of producing carbide. It is known that high-chromium alloys absorb nitrogen at high temperatures with avidity when they have the opportunity, and it is conceivable that, as a result of variation in furnace operation, the nitrogen content of individual casts of " 18–8 " steels may vary appreciably. If such casts were treated with the same amount of titanium, a varying fraction of the latter would be rendered inoperative.

Columbium is claimed to be oxidised less readily than titanium, and thus to overcome the main disadvantages of the latter alloy. It forms a carbide similar to TiC, but owing to its greater atomic weight (93 as against 48) it must be added in an amount at least eight times the carbon content of the steel in order that there may be sufficient to combine, even theoretically, with all the carbon.

Although the use of columbium as a preventive for intergranular corrosion originated in the Krupp Research Laboratory,[31] where its advantage of being less readily oxidised was pointed out, much of its development as a practical steelmaking alloy has taken place in the United States, its properties and advantages being described in several publications.[32] It forms a stable carbide only slightly soluble at high temperatures in the chromium-

31 British patent 386690, January, 1933. The corresponding German patent was granted in 1930.
32 " Effects of Columbium in Chromium-Nickel Steels." F. M. Becket and R. Franks. Trans. Am. Inst. Met. Eng., vol. 113, 1934, p. 143.
" Titanium and Columbium in Plain Chromium Steels." F. M. Becket and R. Franks. Trans. Am. Inst. Min. Met. Eng., vol. 113, 1934, p. 126.
" Effects of Special Alloy Additions to Stainless Steels." R. Franks. Trans. Am. Soc. Metals, XXVII (1939), p. 505.
" The Effect of Molybdenum and Columbium on the Structure, Physical Properties and Corrosion Resistance of Austenitic Stainless Steels." R. Franks, W. O. Binder, and C. R. Bishop. Trans. Am. Soc. Metals, XXIX (1941), p. 35.

nickel austenite, less soluble, it is claimed, than titanium carbide. Thus Franks[32] states that if the columbium : carbon ratio exceeds 10, complete immunity from intergranular corrosion is obtained in material normally softened at 1,100° C. without any stabilising treatment, though the latter is necessary if the ratio falls to 8 or lower. In the discussion on this paper, however, Dr. Aborn stated that a stabilising treatment at 800°–900° C., designed to achieve maximum formation of the special carbide, improved the columbium-bearing steel precisely as it improved the titanium product. Probably there is little difference in the behaviour of the two alloys in this respect.

As regards ease of oxidation, Dr. J. C. Hodge[33] states that approximately 40% of the original columbium content of an electrode is lost during metal arc deposition, which compares favourably with the 60% or more of titanium oxidised in similar circumstances. Dr. Mathews[34] recommended that the columbium : carbon ratio of electrodes should be at least 10 : 1, so that enough columbium would remain in the deposited metal to ensure resistance to intergranular attack during subsequent reheating in crossed welds. It would appear, therefore, that an electrode or filler rod containing an adequate amount of columbium is likely to produce weld metal freer from intergranular susceptibility than an electrode or rod which depends solely on a titanium addition for this purpose ; the deposit from the columbium steel, however, would probably not be completely free from intergranular susceptibility if heated for long periods at, for example, 650° C.

Tantalum has been claimed[31] to act in the same way as columbium, but more is required to produce a similar effect as a result of its higher atomic weight, 181, which necessitates a Ta : C ratio of 15 : 1, to form the carbide TaC. Tantalum and columbium frequently occur together in nature, and they are difficult to separate, even in the laboratory. Some varieties of " ferrocolumbium " which have been marketed have contained appreciable amounts of tantalum, the two being bracketed together in analytical reports as " Cl + Ta " ; in some samples the amounts of the two metals have been about equal. The presence of this tantalum would necessitate a greater addition of alloy than if the latter was a pure ferrocolumbium, owing to the greater atomic weight of the tantalum. In the original Krupp patent[31] it is claimed that tantalum, like columbium, is not greatly oxidised during welding. Prof. Maurer also makes a similar claim.[35] On the other hand, Dr. Kinzel, of Union Carbide and Carbon Research Laboratories Inc., has stated[36] that tantalum is more easily oxidised during welding operations than titanium. Owing to its high cost and the relatively large amounts required to produce like effects as compared with carbide-forming metals of lower atomic weight, tantalum is at present hardly likely to be of much practical importance as an antidote to intergranular corrosion, except as a more or less unavoidable constituent of ferro-columbium. If Dr. Kinzel's opinion as to its rate of oxidation should be confirmed, this would be a further handicap to its use.

(*To be continued.*)

Monel Notes

The current issue of this publication contains a summary of electric-welding practice with Monel, nickel and Inconel ; instructions for the production of a pressed Monel component ; some notes on bearing materials for Monel ; and some data on Thermometal. A method of distinguishing Monel and nickel from other metals is also outlined. The issue contains much practical information which should be particularly useful at the present time. Copies may be obtained, free of charge, from Henry Wiggin and Co., Ltd., Grosvenor House, Park Lane, London, W. 1.

33 " The Book of Stainless Steels." Edited by E. Thum. 2nd Edition, p. 197.
34 *ibid.*, p. 457.
31 British Patent 386690. (F. Krupp, A.-G.) January, 1933. The corresponding German patent was granted in 1930.
35 " High Chromium Irons and Steels." E. Maurer. *Metal Progress*, XXXI (1937), p. 535.
36 Private communication.

Tin and Tin Uses

The latest issue of the Tin Research Institute's quarterly review gives details of some improved pewter alloys containing over 90% of tin, which have all the merits of malleability and attractive sheen associated with the usual pewter alloys, but are substantially stronger. Spinning and other fabricating operations are as easily carried out as with ordinary pewter, but when finished articles of the new pewter are given a simple heat-treatment they develop 70 to 80% greater strength, and this strength is permanently retained in service conditions.

An article on electro-tinning contrasts the old-fashioned stannous chloride bath with modern plating baths ; it is shown that the former bath is of value only for producing very thin tin coatings of bright appearance, but modern baths will give tin coatings of any thickness desired, and so are of particular value for food-processing equipment. Another article dealt with opacifiers for vitreous enamels in which it is indicated that the special qualities of tin oxide have enabled it to maintain its position in the enamelling industry.

An example of the value of tin as a protective coating on steel is provided by its use in connection with the nitriding process, in which surfaces to be kept in an unhardened state are protected by a layer of tin. Nitriding is applied to cylinders, crankshafts, gears, shacklepins and valve sleeves for aero, automobile and Diesel engines, as well as to textile, cement and plastic-moulding machinery. Reference is also made to a simple but sensitive chemical test for identifying tin in white-metal scrap, and of special tin solders which have higher melting points and greater strength than the usual tin-lead alloys.

Copies may be obtained free of charge on application to the Tin Research Institute, Fraser Road, Greenford, Middlesex.

British Society of International Bibliography

THE first meeting of the new session of the above Society takes the form of a joint discussion on the subjects of the " Preparation of Subject Indexes to Volumes of Periodicals " and the " Listing of Titles of Periodical Publications." Dr. S. C. Bradford, F.L.A., will open the discussion on the former subject and Mr. E. Lancaster-Jones on the latter.

The meeting will be held at the Institution of Electrical Engineers, Savoy Place, Victoria Embankment, London, W.C.2, on September 26th, 1941, at 2·0 p.m. A light buffet lunch will be provided at 1·0 p.m., at a cost of 1s. 6d. per head (which charge will also include tea following the afternoon meeting. Will members and others wishing to participate in the lunch send a written notification of their intention, enclosing 1s. 6d. payment in advance, to Mr. J. F. Stanley, British Standards Institution, 28, Victoria Street, London, S.W.1.

Substitute for Baling Wire

In order to conserve supplies of steel, British Ropes, Ltd., who are large manufacturers of baling wire, have developed a substitute for baling wire called " Balax." It is a fibre substitute, and its use effects a saving of something over 20% in baling costs owing to the fact that there is three times more yardage in a ton of Balax than there is in a ton of baling wire.

Balax has now been used by councils, public authorities, and industrial firms for some considerable time, but the production of this substitute is now subject to the Hemp Control Section of the Ministry of Supply, and British Ropes, Ltd., have to obtain a licence to spin the amount of any order ; generally speaking, however, the Hemp Control are willing to authorise the spinning of three months' supply for any user whose stock of Balax is small, provided that a Ministry of Supply form is completed and sent to British Ropes, Ltd., Anchor and Hope Lane, Charlton, London, S.E. 7.

ERRATUM

In our reference to the Annual Autumn Meeting of the Institute of Metals on this page, it is erroneously stated that the President, Lieut-Col. R. M. PRESTON, D.S.O. occupied the Chair and the error was only noted after the issue came off the press. Actually DR. C. H. DESCH, F.R.S., Past-President occupied the Chair in the absence abroad of the President.

The Institute of Metals

Annual Autumn Meeting in London

THE thirty-third annual autumn meeting was held at the offices of the Institute, Grosvenor Gardens, London, S.W1, on September 17, with Lieut.-Col. the Hon. R. M. Preston, D.S.O., in the chair. The initial business meeting was commenced with the approval of the minutes of the previous general meeting; nomination of officers for 1942; the announcement of election of members and student members; and other business of the Institute. At this meeting the Council nominated the following members as officers of the Institute for 1941-42: *President*: Lieut.-Col. Sir John Greenly, K.C.M.G., C.B.E., M.A. *Vice-Presidents*: Mr. Horace W. Clarke, Mr. H. S. Tasker, B.A. *Members of Council*: Mr. G. Wesley Austin, O.B.E., M.Sc., Mr. W. F. Brazener, Mr. H. W. G. Hignett, B.Sc.

At the conclusion of the formal business meeting several papers were presented for discussion. These included " Causes of Porosity in Tin-Bronze Castings "; " Unsoundness of Gravity Die-Cast Silicon-Aluminium Alloy Pistons "; " The Influence of Crystal Structure on the Cold-Rolling and Annealing of Copper Strip "; and " X-Ray Examination of the Crystal Structures of Rolled Magnesium and a Magnesium Alloy." A significant fact in these papers is their practical character, and brief reference to them here will be of interest.

Causes of Porosity in Tin-Bronze Castings

While the tin-bronzes are recognised as liable to unsoundness resulting from shrinkage and gas evolution, no extensive and co-ordinated study have previously been reported on the causes and extent of such unsoundness. This paper, by T. F. Pearson and W. A. Baker, is confined to this aspect of bronze founding. It embraces the results of extensive tests which have been made to determine the influence of shrinkage and of dissolved gases on the incidence of porosity in tin-bronze, using a melting and casting technique which permitted very close control of all conditions, which yielded strictly comparable results. The degree of porosity was estimated from density measurements and tensile tests were made on castings.

The bronzes are very prone to dispersed shrinkage unsoundness by reason of the long freezing range of the alloys. This unsoundness often appears as tortuous interdendritic fissures, which have comparatively little effect on density but are very detrimental to mechanical properties. The alloys are also prone to unsoundness resulting from the evolution of hydrogen, water vapour, carbon monoxide and sulphur dioxide, the extent of the gas porosity being greatest from the first-mentioned two causes and very much less marked from the last-mentioned gases. Carbon dioxide and nitrogen are inert to the alloys. Gas porosity generally takes the same form as shrinkage unsoundness except in grossly unsound castings, where the cavities may appear approximately spherical in shape.

The reaction between water vapour and molten bronze is reversible, and it is shown that oxidation and/or deoxidation are effective for the purpose of preventing or minimising unsoundness resulting from exposure of melts to moist atmospheres. The generally accepted practice of melting in slightly oxidising atmospheres is thus justified. The evidence indicates, however, that elements with a high affinity for oxygen, such for example as phosphorus, will, if present, hinder the expulsion of reducing gases by oxidation. This investigation is described more fully elsewhere in this issue.

Unsoundness of Gravity Die-Cast Silicon-Aluminium Alloy Pistons

Another aspect of unsoundness is discussed in this paper by R. T. Parker, which deals with unsoundness of aluminium alloy pistons, particularly in the skirts of small 12 per cent. silicon-aluminium alloy pistons. The unsoundness took the form of fine cavities, revealed after machining the surface, in positions remote from the runner and riser. In the investigation on the subject, which is described, the factors kept in mind in attacking the problem were gas contamination, machining technique, and temperature of the die-assembly in which the pistons were cast.

Comparison of atmospheric conditions with the percentage of scrap obtained in the foundry showed only a vague relationship. Over periods of some weeks increases in atmospheric humidity were followed by general increases in percentage of scrap, while in several instances sharp daily variations in humidity were followed by sharp changes in the percentage of scrap.

A brief examination of a piston after diamond machining by independent operators showed that small cavities may be disclosed or concealed according to the technique adopted.

Two experiments, in which pistons were cast from metal having a high or low gas content into a die-assembly fitted with thermocouples, demonstrated clearly the effects of variation in the gas content of the metal and temperature of the die-assembly. Of micrographic and X-ray methods of examination, the latter proved far more useful in assessing the soundness of the pistons. A well-marked relationship between soundness and die-assembly temperature was observed, the hotter assembly giving the better results. With metal of both high and low gas content, pistons of reasonable soundness were obtained at higher assembly temperatures; but at lower assembly temperatures the metal of low gas content gave pistons of inferior quality containing localised unsoundness. Pistons from metal of high gas content contained unsoundness of a finer and more general type, owing to the dispersive effect of the gas present.

The variation in gas content, therefore, explained differences in the type of unsoundness observed. Variations in the atmospheric humidity could be admitted as only partially responsible for a hitherto unexplained periodicity in incidence of the unsoundness. Variations in machining technique were considered of much more importance in this respect.

The relationship between die-assembly temperatures and soundness of the pistons points to a way of obtaining an immediate improvement in quality, although a coincidental improvement in quality of the metal is also desirable.

The Influence of Crystal Structure on the Cold-Rolling and Annealing of Copper Strip

The work described in this paper by Dr. Maurice Cook and Dr. T. le Richards concerns a study of the effect of progressively increasing cold-rolling reductions and subsequent annealing on copper strip composed of four different crystal structures. The study was made by X-ray and microscopic methods on H.C. copper strips.

It is shown that the same twin-fibre textures are ultimately developed with increasing rolling reductions in strips possessing all four types of initial structure. The degree of preferred orientation of crystals in the strip developed on rolling, although dependent on the degree of preferred orientation before rolling and on the magnitude

of the rolling reduction, is independent of the initial grain-size. Some strips with certain types of structure, and particularly strips having a small grain-size before rolling, showed, after very heavy rolling reductions, self-annealing effects.

The effect of rolling reductions up to about 50 per cent. and subsequent annealing is to develop a random orientation of crystals, but a rolling reduction of about 25 per cent. is necessary to eliminate from the strip any preferred orientation present before rolling. The twin-fibre textures developed in strip rolled with reductions in excess of about 50 per cent. can either recrystallise independently to form a double-texture structure or can coalesce to form a single-texture structure, depending, in general, on the initial grain-size and the magnitude of the final rolling reduction. Increasing the final annealing temperature has, with a few exceptions, little effect on the final structure other than to increase the grain-size of the strip. In certain circumstances, high final rolling reductions and high final annealing temperatures give rise to the development of abnormally large crystals. Pronounced directionality, as shown by tensile tests and earing on cups, is developed under certain conditions, and the two types of directionality noted, as well as the crystal-growth characteristics, have been related to the crystal structure.

X-ray Examination of the Crystal Structures of Rolled Magnesium and a Magnesium Alloy

Specimens of rolled magnesium, of the magnesium alloy Elektron AM503 rolled from cast billets, and of the same alloy rolled from extruded slabs have been examined by transmitted radiation and by the back deflection X-ray method, the results of which are given in this paper by D. E. Thomas. All the specimens show orientation of the hexagonal axis approximately normal to the rolling plane, with random distribution round the axis ; the hexagonal axis, however, showed deviation from the normal of about $\pm 25°$ in the direction of rolling and $\pm 15°$ in the transverse direction.

The orientation is more fully developed in the Elektron alloy than in magnesium. The two types of Elektron gave similar orientations. Recrystallisation and grain growth start at a lower temperature in magnesium than in Elektron and also proceed further. At any given temperature recrystallisation and grain growth proceed further in the more severely cold-rolled specimens. Sharp reflections, indicating well-formed crystals, appear at 200° C. in the more severely cold-rolled magnesium, but do not appear in the Elektron specimens below 300° C. After heating at 500° C. larger crystals are obtained in magnesium than in Elektron.

Quench-Crack Prevention in Ni-Cr-Mo Forgings
By Bernard Thomas, F.Inst.P., F.Inst.F.

Difficulties encountered in heat-treatment are not infrequent; they occasionally involve careful investigation to determine the cause and provide a remedy. Some are encountered as a result of quenching, and in this article the author discusses the prevention of quenching-cracks in nickel-chromium-molybdenum drop forgings.

IN the heat-treatment of ferrous drop forgings, however well-run a plant may be, there occurs periodically a cycle when quenching cracks develop unexpectedly in certain types of work. An analysis of conditions surrounding the difficulty frequently reveals that there has been no change in steel specification, but that a different shape or size of forging has been quenched from the same temperature as was employed for the previous batches.

In occurrences of this nature one may suspect the quenching medium, and if oil, an examination would probably be made to ascertain if contaminated with water. Logically, however, when the trouble is confined to a particular batch, or series of batches, it is much more reasonable to suspect the articles being quenched than the media employed.

Steels to Specifications 4S11 and S65 are probably the two chief offenders in the foregoing respect, and in order to refresh the memory both specified and typical analyses are shown in the accompany tables.

SPECIFICATION 4S11.

	C. %	Si. %	Mn. %	S. %	P. %	Ni. %	Cr. %	Mo. %
Specified	0·25– 0·30	0·30 max.	0·45– 0·70	0·05 max.	0·05 max.	2·75– 3·75	0·50– 1·0	—
Typical :								
A.	0·31	0·24	0·58	0·022	0·020	3·29	0·66	0·25
B.	0·32	0·18	0·45	0·023	0·017	3·29	0·59	0·22
C.	0·29	0·19	0·60	0·031	0·029	3·09	0·88	0·21
D.	0·32	0·17	0·52	0·029	0·034	3·07	0·70	0·20
Average	0·31	0·19	0·54	0·026	0·025	3·19	0·71	0·22

The specification allows at the option of the steelmaker the following elements to the amounts stated : Vanadium 0·25%, Molybdenum 0·65%, and Tungsten 1·0%.

SPECIFICATION S65.

	C. %	Si. %	Mn. %	S. %	P. %	Ni. %	Cr. %	Mo. %
Specified	0·22– 0·28	0·30 max.	0·35– 0·65	0·05 max.	0·05 max.	2·75– 3·5	1·0– 1·4	—
Typical :								
A.	0·26	0·205	0·46	0·040	0·032	2·97	1·18	0·27
B.	0·26	0·205	0·45	0·053	0·027	2·92	1·22	0·25
C.	0·26	0·30	0·50	0·043	0·044	2·95	1·38	0·28
D.	0·25	0·25	0·47	0·046	0·036	3·00	1·21	0·29
Average	0·26	0·24	0·47	0·041	0·035	2·96	1·25	0·27

The specification allows at the option of the steelmaker the following elements to the amounts stated : Vanadium 0·25%, Molybdenum 0·65%, and Tungsten 1·00%.

Superficially, one would expect satisfactory results from analyses of the nature indicated, but experience has shown that this is no sinecure. Again, the higher average chromium content of the S65 would appear to render it more likely to crack on quenching than the 4S11, but apparently the higher carbon and nickel of the latter outweighs the chromium with consequent detrimental effects.

Ignoring mechanical defects due either to steel or forging production, both of which are capable of giving a lead for quench-cracks, there can be no doubt that the main cause of cracking is internal stresses.

Resorting to an elementary description on quenching a forging, the outer case of " skin " is chilled first while the inner portion retains its heat. If the component be small, say less than 2 in. maximum thickness, the chilling process will continue unhindered until the whole mass is quenched in a reasonably uniform manner. If, however, the thickness exceeds 2 in., the risk increases measurably as the quenching effect begins to tail off, leaving the hot interior able to attempt to reheat the portion already chilled. The stresses thus set-up by the irregular temperature are sometimes sufficient to cause rupture, which need not necessarily be on the outside surface. A recent experience on 4S11 forgings of 4 in. thickness showed that stress cracks were present after hardening at $\frac{3}{8}$ in. below the outer face, and examination does not reveal these until machining has taken place.

It has been stated that a cure is to arrange for slow cooling between temperatures of 400° and 200° C. While it may be feasible to arrange this for odd forgings of intermittent character, it becomes a much more difficult matter for production on a large scale, and other expedients become necessary.

After a number of exasperating occurrences in the past, the writer determined to solve the trouble. Eliminating in the first all extraneous causes, the remainder were each studied carefully and an assimilation of facts made until sufficient data were available for the purpose. Care was taken to ensure that as many varieties of forgings as

Causes of Porosity in Tin-Bronze Castings

By T. F. Pearson, M.Sc., and W. A. Baker, B.Sc.

Extensive tests have been made to determine the influence of shrinkage and of dissolved gases on the incidence of porosity in tin-bronze, using a melting and casting technique which permitted very close control of all conditions and yielded strictly comparable test results. The degree of porosity was estimated from density measurements and tensile tests were made on the castings. The technique employed and the results obtained are discussed in a paper at the Thirty-third Annual Autumn Meeting of the Institute of Metals. An abridgement is given here.

LITERATURE relating to the melting and casting of bronzes is very extensive, and information on various points, such as the properties and soundness of bronze castings, the effect of impurities and of the melting and casting technique employed in their production, is scattered throughout a large number of papers and articles, most of which relate to a particular alloy or casting. Thus, while the alloys are recognised as liable to unsoundness resulting from shrinkage and gas evolution, no extensive and co-ordinated study has previously been reported on the causes and extent of such unsoundness. The object of the investi-gation reported in the present paper was to clarify this unsatisfactory position by a correlated study of the influence of shrinkage and of dissolved gases on the soundness and hence the properties of bronze castings. The term un-soundness is used throughout in a limited sense—i.e., to indicate the extent of porosity in a casting. The experi-mental work was confined to copper-tin and copper-tin-phosphorus alloys, and it was anticipated that the results would be applicable to the variety of more complex bronze alloys in common use.

Castings were first prepared as free as possible from porosity, due either to shrinkage or to gas evolution. In these and subsequent experiments observations were made on the effect of shrinkage on the properties of substantially gas-free castings, and an extensive study was then made of the influence of melting and casting in various gases on the soundness and tensile properties of castings.

Alloys of the composition 90 : 10 copper-tin and 89·5 : 10 : 0·5 copper-tin-phosphorus were prepared from (1) oxygen-free copper supplied as 1¾ in. diameter, bright-turned bar, containing less than 0·01% total impurities ; (2) Chempur, containing 0·015% total impurities ; and (3) phosphor-copper, containing 14% phosphorus, prepared from cathode copper and pure red phosphorus. Analysis of early ingots agreed very closely with the intended com-positions and the accuracy of weighing of the charge was relied upon in subsequent experiments.

Melting and solidification was carried out in a closed tube placed in the field of a high-frequency induction furnace. The apparatus in Fig. 1 consisted essentially of a vertical silica tube of 2½ in. internal diameter and 3 ft. long, sealed at both ends with water-cooled copper heads fitted with rubber washers. The tube was exhausted with a Hyvac oil pump for melting under reduced pressure ; alternatively, controlled gas atmospheres were admitted through the bottom seal. Tapered chill- or sand-cast bars were top-poured via the bottom-pouring magnesia crucible supported in the high-frequency field above the mould. Facilities were provided for making temperature measure-ments. The time required to pour the melt was estimated by observation through a window in the top head. The rate of pouring was adjusted in preliminary experiments ; in the experiments described in the paper melts were poured through a ⅛ in. diameter hole. The pouring time was then 16 to 18 seconds.

Copper moulds were used and dry sand moulds of the same internal dimensions were rammed in vented steel tubes, using a mixture containing 100 parts of washed silica sand, 5 parts Bentonite, and 5 parts water. The sand moulds were dried for 2 hours at 250° C. before use. Moulds were preheated to 100° C, before use to drive off absorbed moisture, and the copper mould was coated with acetylene soot. Moulds were at 20° to 30° C. when inserted in the tube and were not perceptibly heated during the melting period, except when moist atmospheres were used, when the whole of the furnace tube and contents were preheated to 100° to 120° C. by external heaters, to avoid condensation of the moisture.

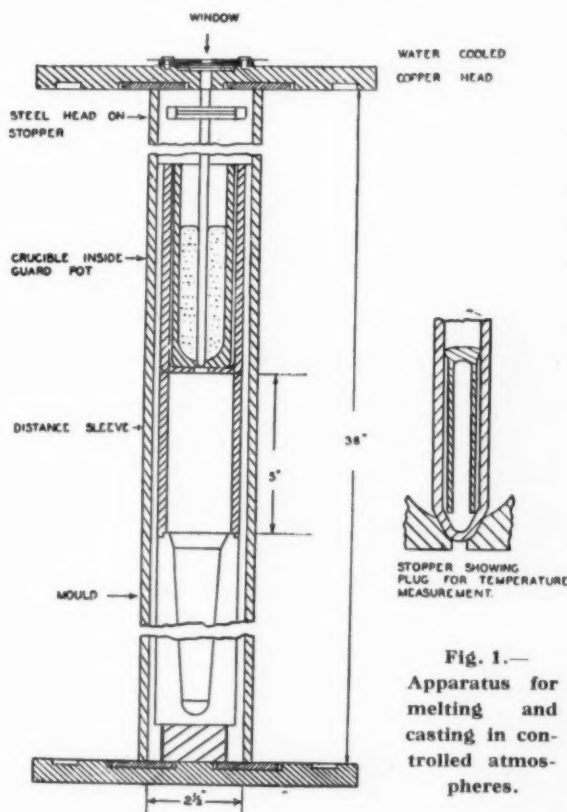Melts were prepared and cast under reduced pressure, and in the following gas atmospheres, dry nitrogen, moist

Fig. 1.—Apparatus for melting and casting in con-trolled atmos-pheres.

nitrogen, nitrogen-sulphur dioxide mixtures, nitrogen-carbon dioxide mixtures, nitrogen-hydrogen mixtures, and carbon-monoxide.

The charge was melted as rapidly as possible (15 mins.), superheated in about 3 mins. to the desired temperature and maintained at that temperature for a predetermined time (15 mins. unless otherwise stated) in the case of gas treat-ments, or for the time required to secure a suitable vacuum (60 to 70 mins.) when melting under reduced pressure.

The pressures just before and just after casting were 0·03 mm. and 0·5 mm. mercury respectively. The maximum temperature attained in melting coincided in all cases with the pouring temperature.

In some cases melts were deoxidised just before pouring. The deoxidant, phosphor-copper or aluminium, was attached to a copper wire carried in a sleeve bound to the stopper rod. The deoxidant was thus held above the crucible and was plunged into the melt when required, by pushing the wire down. Some charges were oxidised with dry air by connecting the top head to a Hyvac pump and drawing dry air into the bottom of the tube via silica gel driers.

The ingots obtained weighed approximately 700 grms. and were about 8 in. in length. The density of the whole ingot was first determined : the bottom 5 in. was then cut off, and the density of this portion measured separately. Tensile specimens (0·564 in. diameter on the parallel portion) were machined from these bottom portions of the bars and micro-specimens were taken from the upper parts, adjacent to the bottom 5 in. length. Densities were measured to an accuracy of ± 0·003 grm./c.c. and from the figures obtained, the percentage voids in the casting were calculated, using 8·96 grm./c.c. as the maximum density of 90 : 10 copper-tin bronze in the homogeneised condition. Allen[2] has shown that the maximum density of copper-tin alloys with a duplex structure is practically constant at 8·92 to 8·93 grm./c.c. over the range 0 to 14% tin. In this work castings of 90 : 10 copper-tin bronze with a density of 8·92 grm./c.c. have appeared perfectly sound under the microscope, and it follows that the figure of 8·96 used as a standard gives slightly high values for percentage voids. Thus, in all cases the recorded percentage of voids may be 0·3 to 0·4 too high.

The experimental results are presented by seven graphs, in which the properties of the castings are plotted against pouring temperature in a given atmosphere, or alternatively against composition of the atmosphere, the pouring temperature being constant. In the latter case the axis points on the curves were derived from the curves representing melts in pure dry hydrogen.

Microscopic examination showed that the unsoundness appeared as fine interdendritic fissures with or without larger convex-sided cavities. Thus, in chill castings and in sand castings with comparatively small quantities of voids the unsoundness was mainly of the fissure type, and it should be noted that this extremely harmful type of porosity occurred not only in gassy castings, but also in castings prepared under reduced pressure or in an inert atmosphere of nitrogen. In sand castings exhibiting greater unsoundness both fissures and convex-sided cavities were present, and in the grossly unsound sand castings, resulting from exposure of 90 : 10 tin-bronze to moist nitrogen for 45 mins., some spherical porosity was present.

The important fact arising from these observations is that in general no distinction was observed between cavities produced by shrinkage and cavities due to gas evolution, even when the extent of gas unsoundness was such as seriously to impair tensile properties. The unsoundness produced by melting in atmospheres containing sulphur dioxide was exceptional in that it was characterised by the presence of small spherical cavities in or intimately associated with the eutectoid particles. Unsoundness produced by dissolved gases generally tended to distribute the porosity, which instead of being concentrated in the centre of the section in some cases extended to the skin of the casting.

Discussion of Results
A 90 : 10 Copper-Tin Bronze

1. *Melts under Reduced Pressure and in Dry Nitrogen.*—Preliminary experiments showed that very slow pouring, in fact the slowest compatible with emptying the crucible, secured maximum soundness in the top-poured chill castings. Such castings poured under reduced pressure or in an inert atmosphere of nitrogen through a ⅛ in. diameter

hole were practically free from unsoundness, but it is to be noted that the trace of porosity present occurred mainly as intercrystalline fissures. Pouring temperature had little effect except at the extreme higher ranges, where a slightly increased unsoundness was observed. Sand castings poured at the same rate were much more unsound and the degree of unsoundness increased with increasing pouring temperature throughout the range of temperatures used. The degree of unsoundness was considerably greater in the upper portions of the castings, particularly in the case of sand castings.

These observations can be explained by assuming that contraction on solidification was responsible for the porosity. Thus, in the chill castings, the ideal conditions requisite for maximum soundness were achieved—that is, a shallow zone of mixed solid and liquid covered by a small head of liquid metal was maintained by slow pouring throughout the formation of the ingot. In the sand castings, where the rate of heat abstraction was much lower, these conditions did not hold, and the zone of mixed liquid and solid was of such depth that adequate feeding could not take place.

The tensile strengths of the substantially gas-free chill castings were rather erratic, but there was a noticeable trend towards lower values at the higher pouring temperatures. The occasional poor values in the lower temperature range were no doubt due to local concentrations of shrinkage unsoundness. The maximum strength of the chill-cast 90 : 10 copper-tin alloy appeared to be 25 tons per sq. in., and the maximum elongation 20% on $4\sqrt{A}$.

Sand castings, containing up to 2% voids, had consistently good tensile properties, the maximum being approximately 21 tons per sq. in. tensile strength and 24% elongation on $4\sqrt{A}$.

2. *Melts in Nitrogen-Hydrogen Mixtures.*—The effect of a moderate amount of dissolved hydrogen on chill-cast bronze was notable. The castings produced in an atmosphere containing 11% hydrogen were very slightly less sound than bars produced in nitrogen or under reduced pressure, but their mechanical properties were consistently excellent. The observations may be explained by assuming that the bulk of the dissolved gas was retained in solid solution during the very rapid solidification, and that the small amount rejected during solidification distributed the voids more uniformly across the section, thus improving the properties of the central portion from which the tensile specimen was subsequently machined.

A larger concentration of hydrogen in the melting atmosphere (30·6% hydrogen) produced gross unsoundness in the chill castings and seriously impaired their tensile properties, particularly as the casting temperature was increased. Sieverts'[1] work on gas solubility indicates that the relation between hydrogen content of the melt and temperature, given a particular concentration of hydrogen in the melting atmosphere, would be defined by a curve. Accepting this, it is clear that if only the gas evolved during solidification were trapped, the extent of gas unsoundness would be independent of treatment and casting temperature and would have a constant value determined by the change in solubility over the freezing range. Curves in two of the graphs show, however, that the unsoundness increases rapidly with pouring temperature, and it follows that part at least of the gas soluble at higher temperatures was trapped in the chill castings.

Sand castings prepared in nitrogen-hydrogen mixtures were much more unsound than the corresponding chill castings, 11% of hydrogen in the melting atmosphere resulting in unsoundness equal to about twice that which would have resulted from shrinkage. It is highly probable that the comparatively slow cooling in sand moulds permitted escape of the bulk of the gas soluble above the liquidus and that the observed unsoundness was mainly due to the change in solubility of hydrogen over the freezing range. If this is assumed to be the case where the extent of unsoundness was independent of casting temperature—

i.e., bars cast at 1,080° to 1,150° C. in an atmosphere containing 11% hydrogen—the voids in the castings provide an approximate measure or the change in solubility over the freezing range. Thus, assuming that all the gas rejected during this change was trapped and that it exerted atmospheric pressure at the solidus temperature, the change in solubility of hydrogen (in a hydrogen atmosphere of 760 mm. mercury pressure) is of the order of 0·3 c.c./100 grms. metal. This figure is probably low, in fact it is so much lower than the accepted figure, 3·3 c.c./100 grms. for pure copper, as to suggest that a large part of the gas evolved during freezing also escaped from the castings.

The tensile properties of the sand castings prepared in the atmosphere containing 11% hydrogen were very poor, and those of the bars prepared in the atmosphere containing 30·6% hydrogen were much worse, of the order of 9 tons per sq. in. tensile strength and 4% elongation on $4\sqrt{A}$.

3. *Melts in Dry Carbon Monoxide.*—Three chill castings were prepared in a pure carbon monoxide atmosphere, casting at 1,140° C. The bars were very sound, the average properties being 0·5% voids in the bottom 5 in. portion, tensile strength 25·1 tons per sq. in., and elongation 24% on $4\sqrt{A}$. Thus the chill castings did not indicate any solubility of carbon monoxide, but the sand castings show that the gas is slightly soluble. The degree of unsoundness resulting from exposure of the melt to a 100% atmosphere of the gas was considerably less than that produced by exposure to an atmosphere containing only 11% of hydrogen. The tensile properties of the sand castings were not seriously impaired by this moderate gas unsoundness, in fact the bars cast at high temperatures were superior to corresponding bars cast in nitrogen. This effect can probably be ascribed to the more uniform distribution of voids, which as stated previously tended to result from gas evolution.

4. *Melts in Dry Carbon Dioxide.*—Charges melted and chill-cast at 1,140° C. and charges sand-cast at 1,050° C. in nitrogen-carbon dioxide mixtures and in 100% atmospheres of pure carbon dioxide gave castings similar to those cast in nitrogen. Thus the average properties of the chill castings were 0·8% voids in the bottom 5 in. portion, 20·8 tons per sq. in. tensile strength, and 11% elongation on $4\sqrt{A}$, while the sand castings averaged 1·2% voids in the bottom 5 in. portion, 20·0 tons per sq. in. tensile strength, and 17% elongation on $4\sqrt{A}$.

It is generally held that compound gases are dissociated on solution in molten metals, and it is shown in this paper that hydrogen and oxygen co-exist in solution in molten bronze and may recombine and be evolved as water vapour on solidification. It is very probable that carbon monoxide behaves in the same way, and if this is accepted the inertness of carbon dioxide can be ascribed to the preponderance of oxygen in the gas and the resulting tendency to oxidise the melt and prevent absorption of carbon. No attempt was made to verify this suggestion by analyses for carbon content, etc., since the observed effect of dissolved carbon monoxide was small and therefore unimportant in comparison with the effect of hydrogen and water vapour.

5. *Melts in Nitrogen-Water Vapour Mixtures.*—In melting and casting in moist atmospheres, the soundness of chill and sand castings presented similar features. The experiments showed an unmistakable tendency for the gas porosity to approach a maximum at a moisture concentration of 2 to 2·5%. This figure is of course significant only under the particular experimental conditions employed; the critical point is displaced to a higher moisture concentration when the melt is exposed for a longer time. Further, in the discussion which follows it must be borne in mind that the experimental conditions were not such as to allow equilibrium to be attained between melt and atmosphere; thus, if, as is suggested, the moisture was dissociated on contact with the melt, some of the liberated hydrogen was swept away from the reaction surface by the stream of moist nitrogen passing through the furnace tube.

Considering now the mechanism by which the unsoundness was produced, it is apparent that, if the unsoundness were due only to solution and subsequent liberation of the hydrogen formed by dissociation of the moisture, the extent of unsoundness would have steadily increased with increasing moisture concentration. The maxima and minima in the unsoundness curves actually found clearly indicate that another factor operates and, in fact, the curves can only be explained by assuming that both oxygen and hydrogen are dissolved by the melt and that an equilibrium exists between their concentrations in the melt.

Confirmation of this conclusion is given by result, which shows the effects of oxidation and deoxidation on melts previously exposed to moist nitrogen for 45 mins. Additions of phosphorus and aluminium just before (1 min.) pouring eliminated the greater part of the unsoundness, and aluminium, which has a greater affinity for oxygen than phosphorus, was the more effective in this respect. Thus it appears that removal of the bulk of the oxygen present, or its conversion to an inert oxide, reduced the quantity of steam formed during solidification and reduced the extent of gas porosity. It should be noted that the concentration or hydrogen in the melt is unlikely to be affected by such additions, and the fact that this hydrogen did not give rise to such severe unsoundness as it would have done in the presence of oxygen indicates that steam evolved during solidification is much more likely to be trapped in the casting than is hydrogen and/or that the solid solubility of hydrogen is considerably increased by removal of oxygen from the melt. Melts oxidised by exposure to dry air (for 3 mins.) after exposure to moist nitrogen similarly gave comparatively sound castings. In this case the oxygen content of the melt was raised to and maintained at its maximum, and in the absence of moisture in the surrounding atmosphere the dissolved hydrogen was displaced from the metal and the amount of steam formed on solidification and the resultant unsoundness were therefore decreased.

The tensile properties of the chill castings prepared in moist atmospheres were very erratic, but on the average were not much worse than those of bars cast in nitrogen. Some of the curves for tensile properties show minima corresponding with the maxima in the voids curve, both for chill and sand castings, but in general the maxima in the porosity curves were not reflected in the curves for tensile properties. The tensile properties of the sand castings were definitely impaired by steam unsoundness, particularly those cast from melts exposed to moisture for the longer period. Oxidation or deoxidation before pouring restored mechanical properties almost to the same values as those of bars cast in nitrogen, although the bars deoxidised with aluminium had rather poor elongations.

6. *Melts in Nitrogen-Sulphur Dioxide Mixtures.*—Melting and chill casting at 1,140° C. in atmospheres containing up to 1·8% sulphur dioxide had no harmful effect on soundness and tensile properties, but atmospheres containing 5 and 10% of the gas increased the voids in the bottom 5 in. portions of the bars to 3% and impaired the tensile properties, in one case lowering the latter to 10·7 tons per sq. in. tensile strength and 4% elongation on $4\sqrt{A}$.

Sand castings from melts treated and poured at 1,050° C., in atmospheres containing up to 4% of sulphur dioxide, were sound, but possessed very poor mechanical properties. No satisfactory explanation is readily apparent for this observation. Castings poured at 1,150° C. exhibited marked gas unsoundness, but nevertheless had very good mechanical properties. It was stated previously that spherical cavities appeared in the eutectoid particles and sulphide inclusions were also associated with this phase, the last liquid portion of the casting. It seems probable that these cavities were due to the evolution of sulphur dioxide, the gas deriving from the dissolved sulphur and oxygen concentrated in the portions last liquid, and the good tensile properties of the castings may have been largely due to some replacement of harmful fissures by the less

harmful spherical cavities. The buttons or skulls left in the crucibles after pouring increased in size with increasing sulphur content of the melt and from this fact and from the longer time taken to pour through the standard $\frac{1}{8}$ in. hole, it was apparent that the presence of sulphur considerably increased the viscosity of the melt. The resultant lower rate of pouring may have promoted more directional freezing in the bar and may thus have contributed to the good tensile properties of the castings. The actual sulphur contents of the castings ranged from 0·013% for a bar prepared in an atmosphere containing 0·31% sulphur dioxide to 0·04% sulphur when the atmosphere contained 3·3% sulphur dioxide.

B. 89.5 : 10 : 0.5 Copper-Tin-Phosphorus Bronze

1. *Melts in a Nitrogen-Hydrogen Mixture.*—Phosphor-bronze of the composition quoted above was melted and sand-cast in an atmosphere containing 11% hydrogen. The melts were treated and poured at temperatures ranging from 1,050° to 1,250° C. and the resulting castings were much more unsound than 90 : 10 copper-tin bronze cast under the same conditions. The unsoundness in the phosphor-bronzes was, in fact, consistently 3·5% voids* higher than in the plain bronzes poured at corresponding temperatures. The phosphor-bronze has a much longer freezing range than the tin-bronze and the more marked gas unsoundness in the former was probably largely due to this factor, the longer freezing range tending to hinder escape of gas from the casting. It is unlikely that the solubility of hydrogen in the melt is much affected by the presence of phosphorus in such amounts.

The mechanical properties of these phosphor-bronzes were very poor, of the order of 10 to 13·5 tons per sq. in. tensile strength and 3 to 8% elongation on $4\sqrt{A}$. Similar charges melted and sand-cast in dry nitrogen gave bars with tensile strength and elongation of the order of 20 tons per sq. in. and 18% respectively.

2. *Melts in Moist Nitrogen.*—The unsoundness moisture concentration curve for sand castings of phosphor-bronze cast in moist atmospheres is not so well defined as the curve obtained when straight tin-bronze was cast under the same conditions. Despite the scatter of the results, however, there is a suggestion of a maximum and minimum in the unsoundness-moisture content curve, similar to that found for the plain tin-bronze. This suggests that the phosphorus is not completely effective as a deoxidant, some oxygen remaining in solution in equilibrium with the phosphorus and hydrogen and giving rise to " steam unsoundness " during solidification. This conclusion conforms with the results previously described where it was shown that the addition of a small amount of phosphorus before pouring was less effective than aluminium in preventing " steam unsoundness."

The tensile properties of the castings were quite good, excepting those of the grossly unsound castings prepared in very wet atmospheres.

Conclusions

Examination of small tin-bronze and phosphor-bronze castings prepared under accurately controlled conditions indicates that :—

(i) The alloys are very prone to *shrinkage unsoundness* as a result of their long freezing ranges, and the unsoundness tends to take a very harmful form—namely, interdendritic fissures. This form of porosity can be eliminated largely by strongly directional solidification—e.g., by very slow top-pouring in chill moulds. In sand castings, where the rate of heat abstraction is much lower, feeding is seriously hindered by the growth of dendrites in the solidifying zone, and considerable shrinkage unsoundness is almost inevitable.

(ii) *Gas unsoundness* in cast bronzes may result from the evolution of carbon monoxide, hydrogen, water vapour, or sulphur dioxide during solidification of the alloys.

Carbon monoxide is only slightly soluble, and its presence

in molten bronze does not seriously impair the mechanical properties of the castings.

Small amounts of dissolved hydrogen considerably improve the mechanical properties of chill-cast bronzes, an effect which is ascribed to the distribution of the porosity by moderate gas evolution. Such small amounts of hydrogen, however, seriously increase the unsoundness in sand castings and have a very deleterious effect on their mechanical properties.

Larger amounts of dissolved hydrogen produce gross unsoundness in both chill and sand castings.

Hydrogen and oxygen co-exist together in molten bronzes and recombine during solidification with a resultant evolution of steam. This " steam unsoundness " can be eliminated largely by oxidation to displace hydrogen, or alternatively, by deoxidation to remove oxygen or convert this reactant to an inert oxide. In bronzes containing elements with a high affinity for oxygen—e.g., phosphor-bronzes—the oxygen solubility is likely to be very low, and hence gas unsoundness resulting from exposure of the melt to moisture is probably mainly due to the evolution of hydrogen rather than of steam.

Moderate unsoundness was observed when melts were exposed to sulphur dioxide, and it is likely this also resulted from a reversible reaction, between dissolved oxygen and sulphur. The comparatively good mechanical properties of these unsound castings may be due to the presence of spherical or other cavities less harmful than the fissure type normally observed in bronze castings.

(iii) A notable feature of the experimental results was that while consistent values were generally found for the extent of porosity in castings made under particular conditions, the tensile properties of the castings were erratic. The variable tensile properties are ascribed to local concentrations of porosity, particularly of the interdendritic fissure type, and it is evident that misleading conclusions might easily be drawn from comparisons of tensile properties alone.

(iv) The generally accepted melting practice—namely, melting under oxidising conditions followed by deoxidation before pouring is based on a sound principle—namely, the elimination of reducing gases by oxidation. It is not likely, however, to be completely effective when the molten alloys contain elements having a high affinity for oxygen.

Methods of Joining Monel, Nickel and Inconel

MONEL, nickel and Inconel are all amenable to the normal methods of joining. These fall into two main groups :—

(a) Soft soldering, silver soldering or brazing.

(b) Welding.

As nickel and the nickel alloys are generally used for their corrosion- or heat-resisting properties, welded joints, which avoid the introduction of materials of lower corrosion- or heat-resistance, are preferable to soldered or brazed joints. Nevertheless, there are very many purposes for which either soft- or silver-soldered joints are acceptable, and their simplicity does much to recommend them. For this reason it is important to note that these metals may be readily soft- and silver-soldered. Monel and malleable nickel in particular are very amenable to these processes. With " K " Monel and Inconel, rather more care in fluxing is required, but highly satisfactory soft- or silver-soldered joints may be made without undue difficulty.

The special technique needed for welding these alloys, by both the oxy-acetylene and metallic-arc processes, is described comprehensively in a recent publication. Sections are also included on soft soldering, silver soldering and brazing, together with data on carbon-arc, spot and seam, and flash welding. This is a very useful publication, copies of which may be obtained, free of charge, on application to Henry Wiggin & Co. Ltd., Grosvenor House, Park Lane, London, W.1. Individuals making application are asked to give the name of their firm or state the nature of their interest.

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* Based on a value of 8·87 grms./c.c. for the maximum density of the alloy.
1 A. Sieverts and W. Krumbhaar, *Z. physical. Chem.* 1910, **84**, 277.
2 N. P. Allen, *J. Inst. Metals,* 1930, **43**, 81.

The Constitution of Alloys of Aluminium with Magnesium and Silicon

By H. W. L. Phillips, M.A.

The constitution of alloys of aluminium with 0–5% magnesium and 0–2% silicon has been studied in detail and the position of the binary valleys bounding the primary aluminium phase field has been redetermined. The alloys are studied as slowly cooled, no attempt being made to attain equilibrium conditions. The results of their investigation are reported by Mr. Phillips in an Institute of Metals paper* and reproduced here in an abridged form.

THE investigation, of which this is a report, is one of a series on the constitution of aluminium alloys under conditions of metastable equilibrium such as are likely to be met with in commercial practice. The work has been carried out in the Research Laboratories of the British Aluminium Co. Ltd., under the general direction of Dr. A. G. C. Gwyer, B.Sc.

Previous studies of the constitution of aluminium with magnesium and silicon under equilibrium conditions are reviewed. The conclusions of Hanson and Gayler[3] and of Lonasa[4] have been generally accepted. The vertical section through the constitutional model passing through the aluminium corner and the point representing the composition of the compound Mg_2Si is quasi-binary: it divides the system into two partial systems, the components of which are (1) aluminium, Mg_2Si, and silicon, and (2) aluminium, Mg_2Si and Mg_2Al_3. Both partial systems are eutectiferous, and all of the constituents are appreciably soluble in aluminium in the solid state.

The constitution of the alloys under conditions of structural equilibrium appears to be satisfactorily established, but little is known of their constitution as ordinarily prepared, when equilibrium is not likely to have been reached. Hanson and Gayler[3] made a brief reference to the absence of structural equilibrium in alloys lying in the quasi-binary section: they occasionally observed traces of ternary eutectic in addition to the aluminium and Mg_2Si, the sole presence of which would be required by equilibrium. Mehl, Barrett, and Rhines[7] observed the occurrence of binary compounds of aluminium and magnesium in alloys of the quasi-binary section. It is, of course, well known that eutectics extend over a wider range of compositions in cast alloys than in fully annealed ones, and that the process of taking a constituent into solid solution involves a change in the temperature of the solidus, but information on the magnitude of these effects is rarely available in the literature. Yet such knowledge is frequently of practical importance. Experience has shown that the reheating of a cast block of an alloy of this system for rolling or extrusion is not sufficient for the attainment of equilibrium, and hence the extent to which metastable structures are present and the degree to which they persist determine the maximum temperature at which the material may safely be worked or annealed. Experience has also shown that alloys made up to contain magnesium and silicon in the proportions required to form Mg_2Si almost invariably contain free silicon, and this suggests that the reaction between magnesium and silicon may be a balanced one. If this is so, it is of importance to know how the excess of magnesium is distributed, since a non-uniform distribution may lead to impaired resistance to corrosion, and to the formation of an oxide film of irregular thickness during anodizing.

The present investigation was limited to a study of the alloys under conditions likely to be met with in practice. It was decided, therefore, to study in detail the range silicon 0–2, magnesium 0–5%, since this range includes several alloys of commercial importance. In order to verify some of the temperatures and structures observed, it was necessary to make a redetermination of the position and temperature of the binary valleys bounding the primary-aluminium phase field.

Cooling curves were taken of series of alloys the composition of which varied in steps of approximately 0·25% or 0·5%, and the resulting ingots were sectioned and polished for micro-examination. Quantities of about 200 grm. were used for each curve, and the rate of cooling was, in general, about 8° C. per min. This rate of cooling was identical with that used in previous constitutional investigations,[1,2] and was initially selected as being intermediate between that likely to occur in chill casting and that in sand casting. Temperatures were read by a platinum/platinum–rhodium thermocouple in conjunction with a Carpenter–Stansfield deflection potentiometer. An attempt was made to use lattice-parameter measurements to estimate solid solubility, employing monochromatic radiation and the back-reflection method, but the specimens were too coarsely crystalline to permit of the necessary accuracy of measurement. For the determination of the solidus in alloys the final solidification of which did not take place at one or other of the ternary eutectics, a heating-quench method was used. A small specimen, taken from a cooling-curve ingot and having a rare-metal thermocouple attached to its polished face, was dipped into a bath of Wood metal at a superheat of about 10° C. On attaining the required temperature—a matter of some 30 seconds—the specimen was quenched in water and examined for signs of melting, such as the replacement of a coarse eutectic structure by a fine one, or the balling up of acicular constituents. This method proved successful for all alloys containing more than 0·1% of magnesium or silicon, but not for alloys containing less than this amount of either element. Failure to observe signs of melting may have been due to the difficulty in detecting changes in shape or size of the finely dispersed crystals, to changes in solid solubility even during the short heating period, or to the constituents resolidifying on existing nuclei. In these regions, therefore, the solidus temperatures had to be derived by interpolation.

In preparing the alloys, super-purity aluminium was used, analysing:—

	%
Silicon	0·001
Iron	0·001
Copper	< 0·001
Aluminium	99·998 (by difference)

Silicon, which was added as the element, analysed:—

	%
Iron	1·5
Aluminium	0·42
Titanium	0·04
Silicon	98·04 (by difference)

Magnesium was added in the form of a hardener, made up

* *Jour. Inst. of Metals*, 1941, **67**, 257.

[1] A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1927, **38**, 29.
[2] A. G. C. Gwyer, H. W. L. Phillips and L. Mann, *J. Inst. Metals*, 1928, **40**, 297.
[3] D. Hanson and M. L. V. Gayler, *J. Inst. Metals*, 1921, **26**, 321.
[4] L. Losana, *Metallurgia Italiana*, 1931, **23**, 367.
[5] B. Otani, *Kinzoku no Kenkyu*, 1930, **7**, 666.
[6] E. H. Dix, Jr., F. Keller and R. W. Graham, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1931, 404.
[7] R. F. Mehl, C. S. Barrett and F. N. Rhines, *Trans. Amer. Inst. Min. Met. Eng.*, 1932, **99**, 207.
[8] Unpublished work.
[9] W. Hume-Rothery, "The Structure of Metals and Alloys," *Inst. Metals Mono. and Rep. Series*, 1936 (1), 92.

from super-purity aluminium and electrolytic magnesium, a typical analysis being :—

Magnesium	5·64
Silicon	0·004
Iron	0·001

Micrography of the Alloys

Silicon is readily distinguishable by its characteristic colour and hardness, and needs no etching reagent. Mg_2Si has a characteristic habit, and is pale blue in colour, frequently irridescent, and occasionally tarnished. Like silicon, it needs no etch for its identification. In an unetched section, particularly if present in small amounts, Mg_2Al_3 is almost impossible to distinguish from aluminium. It is readily outlined, and slightly darkened, by a momentary dip in dilute sodium hydroxide solution.
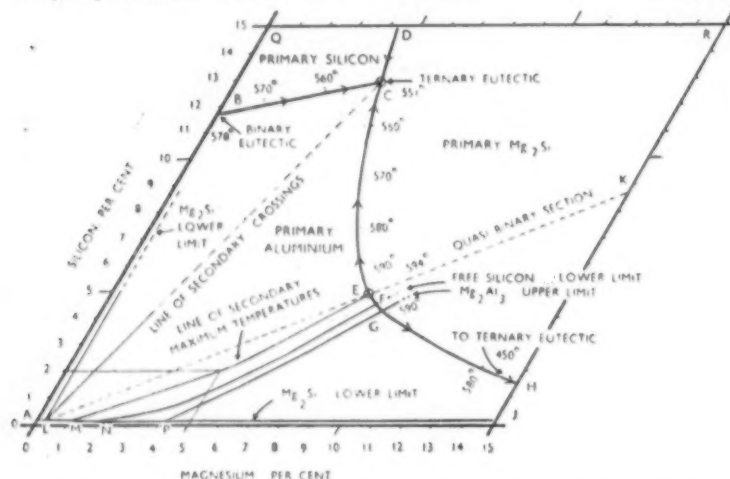

Fig. 1.—Constitution of the alloys as slowly cooled.

Alloys made up from aluminium of ordinary purity were found to contain constituents due to iron, of which four were identified. $FeAl_3$* occurs in alloys having a very low silicon content ; it forms hard crystals of prismatic habit, lavender in colour, and can readily be identified by its etching behaviour, being tinted green by sodium hydroxide solution or brown by hydrofluoric acid. With increasing silicon the constituents a(Fe–Si) and β(Fe–Si) of the aluminium–iron–silicon ternary system make their appearance. In previous publications[1,2] these constituents were termed respectively β and X. The former, a(Fe–Si), usually occurs in its characteristic Chinese script formation : it is tinted a dull brown by either sodium hydroxide or hydrofluoric acid. β(Fe–Si) invariably crystallises in long needles, easy to identify ; it is tinted red-brown by
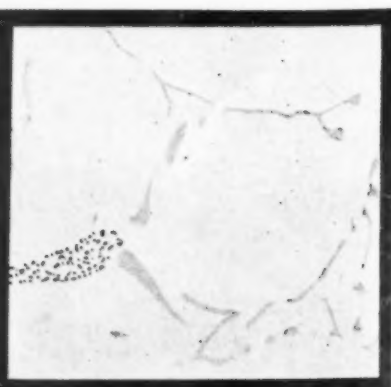
hydrofluoric acid and is but little attacked by sodium hydroxide. In alloys containing much silicon, a pearly grey constituent occurs, which is believed to be a complex containing magnesium, silicon and iron. It has a crystal habit similar to that of Mg_2Si, and is resistant to attack by either hydrofluoric acid or sodium hydroxide. Even at concentrations of iron as low as 0·3%, this constituent forms an intensive primary phase field,[8] separating those due to silicon and Mg_2Si. With aluminium, silicon and Mg_2Si it gives rise to a quaternary eutectic, the composition of which has not been determined but which freezes at 550° C.

General Survey

The constitution of the alloys as slowly cooled is shown in Fig. 1. In the range investigated, three primary phase fields occur, aluminium ($ABCEHJ$), silicon ($BCDQ$), and Mg_2Si ($DCEHR$). The binary valley CEH, separating the primary aluminium and Mg_2Si fields, passes through a flattened maximum E, at 594° C., which appears to coincide with the intersection with the quasi-binary section, AEK. The composition of the ternary eutectic C of aluminium, silicon and Mg_2Si was first determined approximately by micro-examination and extrapolation from cooling-curve arrest temperatures, and then, more accurately, by chemical analysis of samples taken from eutectic areas of micro-sections. Silicon was determined colorimetrically as the yellow silico-molybdic acid complex, using the Pulfrich photometer ; and magnesium gravimetrically as pyrophosphate. The figures obtained were silicon 12·95, magnesium 4·97%. The freezing point was 551° C. The composition of the ternary eutectic of aluminium, Mg_2Si, and Mg_2Al_3 could not be determined. The microstructure of all alloys in the neighbourhood of the invariant point was so coarse and segregated that it was impossible to decide which constituent was primary, or to select eutectic areas for chemical analysis. The eutectic freezes at 450° C.

Free silicon does not disappear at the point E on the binary valley, but persists until the point F is reached. The structure of an alloy in the neighbourhood of F is shown in Fig. 2. A small amount of free silicon is visible in the area photographed, although the amount of magnesium present is more than sufficient to convert the whole of the silicon into Mg_2Si. Mg_2Al_3 first appears in the micro-sections at the point G, giving structures similar to that illustrated in Fig. 3.

In alloys lying within the concentration triangle LCB the secondary separation is that of the aluminium-silicon binary eutectic complex. The isothermals of this secondary

Fig. 2.—Magnesium 8.2, silicon 4.4, iron 0.022%. Unetched × 300.

Fig. 3.—Magnesium 9.3, silicon 4.1, iron 0.023%. Etched in 12½% sodium hydroxide. × 300.

Fig. 8.—Magnesium 2.0, silicon 1.0, iron 0.01%. Unetched. × 300.
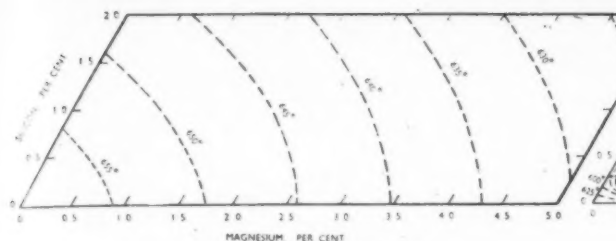

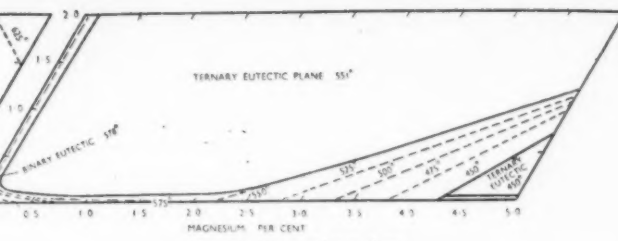Mg_2Si : Half tone. Silicon : Dark particles.
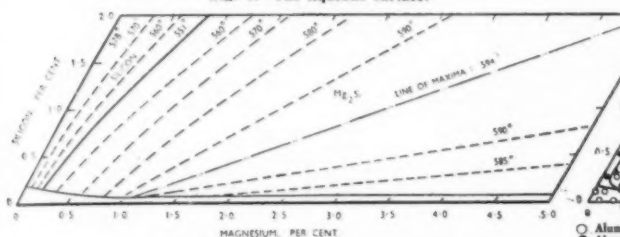
Fig. 4.—The liquidus surface.

Fig. 6.—The solidus surface
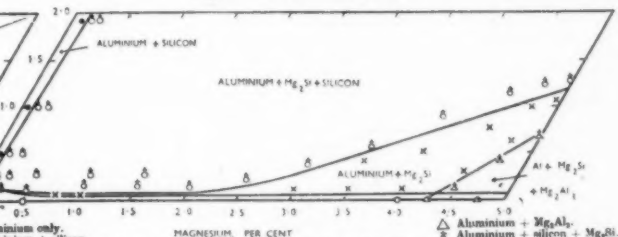
Fig. 5.—The surface of secondary separation.

○ Aluminium only.
● Aluminium + silicon.
× Aluminium + Mg₂Si.

Fig. 7.—Constituents present in solid state

△ Aluminium + Mg₅Al₃.
△ Aluminium + silicon + Mg₂Si.
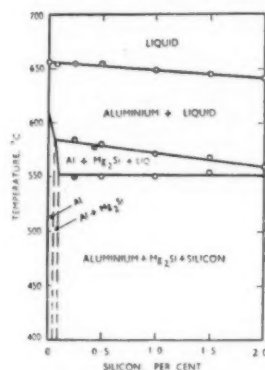▲ Aluminium + Mg₂Si + Mg₅Al₃.
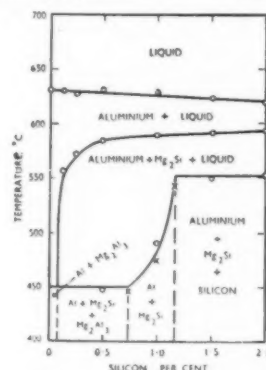
Fig. 9.—Alloys containing 1% magnesium.

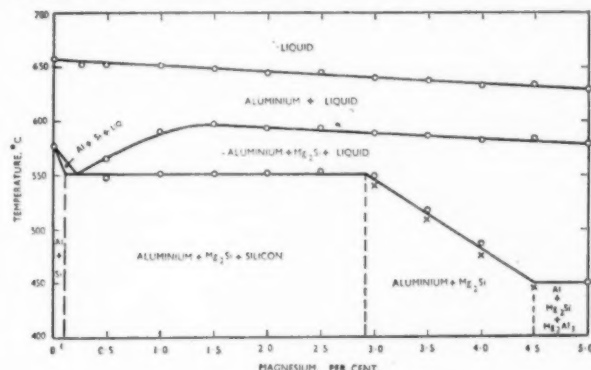Fig. 10.—Alloys containing 5% magnesium.

Fig. 11.—Alloys containing 0.25% silicon.

surface are almost, if not exactly, rectilinear, indicating very little change in the composition of the primary phase during solidification. *LC*, the line in which the secondary surface meets the ternary eutectic plane, is also rectilinear. In the concentration region *ACEHJ* the secondary separation is that of the aluminium–Mg₂Si binary complex. The secondary surface rises to a flattened maximum *ME*, at 594° C., which is neither coincident with the quasi-binary line *AE* nor rectilinear. The curvature of the line *ME* indicates that, under the conditions investigated, the primary phase (aluminium) takes increasing quantities of magnesium into solid solution as solidification proceeds. Under equilibrium conditions, the line of maximum temperatures becomes coincident with the quasi-binary line, *AE*.[3]

In the concentration region *BLNFC* the solidus coincides with the separation of the ternary eutectic of aluminium, Mg₂Si, and silicon : in the region *PGHJ* it coincides with that of the ternary eutectic of aluminium, Mg₂Si, and Mg₂Al₃. As far as can be ascertained, the solidus falls smoothly between these two regions. The line of first appearance of silicon, *NF*, is curved, and its curvature indicates that the ratio of magnesium to silicon dissolved in the primary phase increases as solidification proceeds. Under equilibrium conditions the gap, *NFGP*, between the two ternary eutectic fields widens in both directions, the line of first appearance of silicon moving to the opposite side of the quasi-binary line. The solidus becomes ridge shaped, the ridge coinciding with the secondary ridge along the quasi-binary line.[3]

Under the conditions investigated, aluminium is incapable of dissolving more than 0·2% silicon and more than 4·25% magnesium in the solid state. The solid solubility of Mg₂Si is very small, since the addition of 0·1% of magnesium to aluminium–silicon alloys, or of 0·1% of silicon to aluminium-magnesium alloys is sufficient to

cause the appearance of small but unmistakable crystals of Mg₂Si in the microsections.

The appearance of free silicon in alloys lying on the magnesium side of the quasi-binary line indicates that the reaction between magnesium and silicon has not proceeded to completion, and that magnesium has been taken preferentially into solid solution, thus reducing the amount available for the chemical reaction. In the binary alloys of magnesium and silicon, the maximum in the liquidus at the Mg₂Si composition is rounded,[9] though only slightly, indicating that some dissociation takes place on melting. It appears probable, therefore, that there is a balanced reaction in the liquid phase : $2 Mg + Si \longleftrightarrow Mg_2Si$, and, from mass-action considerations, it follows that the amount of free magnesium in the liquid will be reduced by an excess of silicon, and conversely. This view of the chemistry of the process receives confirmation from the curvature of the isothermals of the surface of secondary crystallisation. On the silicon side of the quasi-binary line the isothermals are almost rectilinear, and their course indicates that the primary aluminium contains little magnesium in solid solution. On the magnesium side, the isothermals are curved, and the magnesium content of the primary phase increases as crystallisation proceeds.

The Range 0–5% Magnesium, 0–2% Silicon

The Liquidus Surface. Detailed comment is unnecessary. The primary constituent is aluminium, and the isothermals are shown in Fig. 4.

The Surface of Secondary Separation. To the left of the diagram (Fig. 5) the secondary separation is that of the aluminium–silicon binary complex. The surface is almost plane, and meets the ternary eutectic horizontal in a straight line—the " line of secondary crossings "—which terminates at the ternary eutectic composition. To the

right of the diagram the secondary separation is that of the aluminium–Mg_2Si binary complex. The surface is ridge-shaped, and slopes very steeply towards the aluminium-magnesium axis of the concentration diagram. In the region magnesium 4–5%, silicon 0–0·1%, the secondary separation is probably that of the aluminium–Mg_2Al_3 complex, freezing at 450° C. It was not possible, however, to determine the line of secondary crossings, or the exact thermal temperature of separation, owing to the small thermal effects and to the prevalence of undercooling. No attempt has therefore been made to plot isothermals below 585° C.

The Solidus Surface (Fig. 6). Direct measurements of the solidus were made on series of alloys containing aluminium, varying quantities of magnesium, and 0%, 0·25%, and 0·50% silicon ; and also on series containing 4·0% and 5·0% magnesium with varying silicon content. Attempts were also made to determine the solidus in a series containing 0·10% silicon, but without success, since it was impossible to distinguish with certainty the first signs of melting. The isothermals in this region have therefore been derived by interpolation.

Another example of the lack of equilibrium in these alloys is furnished by a comparison between the isothermals of the secondary and solidus surfaces. For instance, alloys containing magnesium 2·5%, silicon 0·15% and magnesium 4·7%, silicon 0·40%, both lie on the 585° C. isothermal of the secondary surface, yet the former lies on the line of first appearance of silicon, having its solidus at 551° C., and the latter on the line of first appearance of Mg_2Al_3, with solidus at 450° C. During the secondary

crystallisation, the system should be univariant, and at any temperature the composition of the liquid phase should be fixed. At 585° C., when the secondary separation commences, the liquid phase in both alloys should have the same composition, and this identity of composition should be maintained throughout the remainder of the process of freezing. The two alloys should therefore have the same solidus. This argument, however, is based on the assumption that the solid phase is in equilibrium with the liquid, and this cannot be the case. What probably happens is that, in the alloy containing 2·5% magnesium, the aluminium-rich phase is dissolving magnesium throughout the whole course of freezing, and leaves insufficient to combine with all the silicon, whereas in the alloy containing 4·7% magnesium, the aluminium becomes saturated locally with magnesium and Mg_2Al_3 crystallises out.

Constituents Present in the Solid State (Fig. 7). Little comment is necessary. The greatest difficulty was found in separating the lines of first appearance of Mg_2Si and of silicon in the range of 0·2–2·0% magnesium, and for all practical purposes they may be regarded as coincident. Both constituents appear with as little as 0·1% silicon.

Fig. 8 has been included to show the colour and habit of the constituents Mg_2Si and silicon in aluminium-rich alloys of this system. The alloy contains more magnesium than is required to combine with the whole of the silicon.

Sectional Diagrams (Figs. 9–11). Three typical diagrams have been included. They show, better than the triangular diagrams, the slope of the secondary surfaces, the secondary crossings, and the shape of the solidus.

Beryllium as a Light Metal Constituent

IN METALLURGIA of September, 1940, an investigation by C. B. Sawer and B. Kjellgren,[1] dealing with the properties of pure beryllium and some of the aluminium alloys prepared with it was briefly discussed. Further work supplementing this investigation by adding information of value and bringing certain phases up to date have been dealt recently by C. B. Sawer.[2]

Very little success has resulted from efforts to alloy magnesium with beryllium, as anything exceeding 1% to 2% of magnesium is apparently rejected as vapour, while the beryllium is solidifying at its melting point approximating 1280° C. Somewhat related difficulties are found to attend efforts to alloy aluminium with beryllium, although there is no trouble from the vapour phase. The The aluminium-beryllium eutectic contains only a fraction of a percentage of beryllium, and, if a solid solution exists, it probably contains less than 1% by weight of beryllium. In order to have the two metals alloy in the liquid state, it is necessary to use temperatures which are far beyond those suitable for aluminium, and consequently gas is readily absorbed and acts as a source of most of the ills commonly associated with it in metals. In general, therefore, although it is quite possible to produce ingots large enough for experimental determinations of the properties of beryllium-aluminium alloys, it has not yet been possible to go beyond this laboratory operation.

To the data on alloy containing approximately 28% of beryllium and having a tensile strength of 11·16 tons per sq. in. and a yield point of 8·48 tons per sq. in., published earlier, may now be added the endurance value of 4·91 tons per sq. in. at 20×10^7 cycles. The as-cast structure of this alloy showed the eutectic surrounded by grains of beryllium.

During the past four or five years extensive investigations have been carried out on beryllium-aluminium alloys with a view to the production of a better piston material, and some of the results obtained are now published for the first time. In general, the strength of wrought binary alloys at a definite elongation are 4·5 to 13·5 tons per sq. in. below those of the strong aluminium-base alloys used in aircraft. Such beryllium-aluminium alloys have a higher modulus of elasticity than the aluminium-base alloys, but their creep strength is very low. At the low stress of 2·25 tons per sq. in., binary-aluminium sheet showed four times as much creep as duralumin alloy at five times the stress.

Binary beryllium-aluminium alloys can be improved by adding other constituents, and an improvement in creep strength is obtained in some cases approaching normal. In such alloys where a good elongation is obtained, the strength is low, but the modulus of elasticity is high. At a temperature of 315° C. (600° F.), such as may exist in a piston, these alloys have higher endurance limits and much higher tensile strengths than the materials now in use, and therefore hold out attractive possibilities if they could be made industrially. So far, after two years co-operative research work, this result has not been attained, and except for limited applications which can be made on material from a laboratory scale of production, it has been concluded that beryllium-aluminium alloys are not a commercial proposition. A possibly interesting small use for beryllium in aluminium-base alloys is the claim that in quantities of about 0·005% it restrains oxidation of the molten alloy and refines the grain. Similar quantities added to magnesium-base alloys have been found to increase the corrosion resistance of such alloys.

THE Export Credits Guarantee Department announces that Mr. A. L. Trump, who has for some years been District Manager at the Birmingham Office, has been appointed District Manager at the Department's Bradford Branch, and will take up his duties on the 8th September, 1941.

Mr. E. Edwards has been appointed Branch Manager at the Department's Birmingham Office with effect from the 1st September, 1941.

1 *Metals and Alloys,* 1940, Vol. 11, **6**, pp. 163-167.
2 *Metals and Alloys,* 1941, Vol. 14, **1**, pp. 37-39.

Dolomite Bricks for use in Steel-Works

By T Swinden, D.Met., and J. H. Chesters, Ph.D., B.Sc.

Further replacement of magnesite and chrome-magnesite bricks by dolomite bricks in open-hearth and reheating furnaces would reduce the strain on shipping and leave home-produced magnesite available for positions in which its use is at present essential. The application of dolomite bricks in various positions of fixed open-hearth furnaces is discussed in this communication* as a result of practical tests. They have given good service in these furnaces and also in reheating furnaces. The manufacture of various grades is described.

THE object of this communication to the Iron and Steel Institute from the Central Research Department of The United Steel Companies Ltd. is to draw attention to certain experiences in the use of stable and semi-stable dolomite bricks, and to suggest that in view of the increasingly difficult shipping position even more use should be made of such home-produced refractories. In suggesting such replacement the authors have borne in mind that the present-day furnace depends more than ever on the use of basic refractories in the back wall, front wall and ports for its high rate of steel production, and do not therefore recommend any change that would be likely to result in a loss of output.

The crux of the dolomite brick problem lies in the fact that high temperature calcination (or even electrical fusion) of dolomite does not yield a stable product. Both the magnesia and the lime formed according to the reaction: fusion) of dolomite does not yield a stable product. Both the magnesia and the lime formed according to the reaction:

$$CaCO_3 . MgCO_3 \longrightarrow MgO + CeO + 2CO_2$$
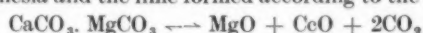
are of moderate crystal size (about 0·05 mm. in dia.), but the lime, unlike the magnesia, hydrates readily, and samples of basic made in this way start to "perish" after only a few days exposure to the atmosphere. The term "dead-burned" dolomite, considered literally, is, therefore, a misnomer, and resort must be had to other means if satisfactory stabilisation is to be obtained.

The ceramic literature of the last twenty years contains numerous suggestions as to how dolomite can be stabilised or the lime fraction removed altogether. Perhaps the first really successful experiments on a works scale were made in Great Britain when, in 1934, bricks containing a 75/25 mixture of dolomite and Sudanite rock[1] (magnesite + talc) were found to give encouraging results in open-hearth furnaces.

Although the modern brick is made with a serpentine addition instead of Sudanite rock, and big improvements have been made in the methods of clinker production, grading, pressing, drying and firing, the general type and composition of all the stable dolomite bricks now in use in Great Britain are essentially similar to those of the bricks made in 1934. Thus, bricks submitted to Messrs. Steel, Peech and Tozer in August, 1935, were shown to have the following properties :—

ANALYSIS					PROPERTIES		
SiO$_2$	..	..	..	13·24%	Porosity	.. .. ..	22·4%
FeO	..	..	..	3·21%	True specific gravity ..	3·2%
Al$_2$O$_3$	..	..	..	1·23%	Refractoriness-under-	
MnO	..	..	..	0·05%	load	25 lb. per in.^{2}
CaO	..	..	..	39·64%	Fail temperature	over 1580° C.
MgO	..	..	..	41·74%		

Comparison of the above results with data given later in this paper for the present-day brick serves to show that even in 1934 the dolomite brick was well on the way to success.

These first bricks were made by firing clots of suitable composition, followed by regrinding, pressing in a small hydraulic press and firing in a baby kiln. They showed a serious brick-to-brick variation and periodically suffered from two serious limitations, viz., hydration in storage and "dusting" in the furnace.

Suggestions had already been made as to the cause of these difficulties, and complete confirmation came in February, 1936, when X-ray examination by Dr. A. H. Jay, of the Central Research Department (The United Steel Companies, Ltd.), in collaboration with Sir Lawrence Bragg, F.R.S., then of Manchester University, showed that the bricks which hydrated contained small amounts of uncombined lime, owing to an insufficient silica content
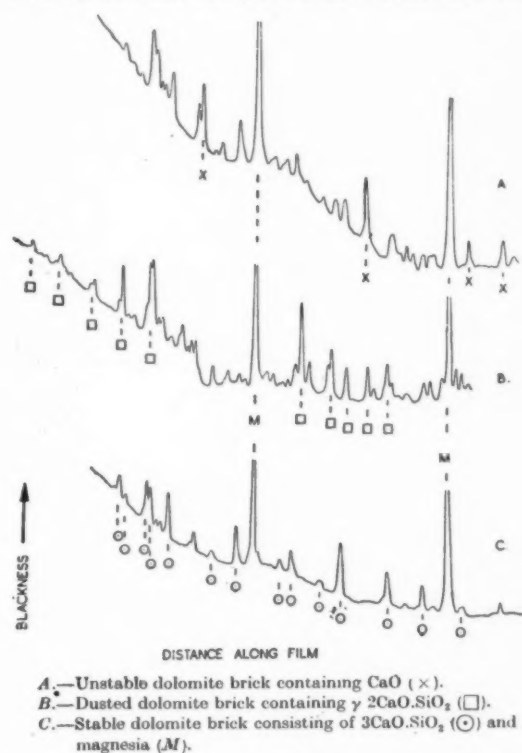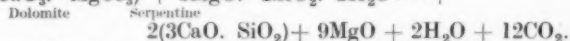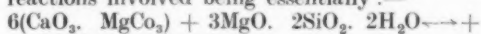

A.—Unstable dolomite brick containing CaO (×).
B.—Dusted dolomite brick containing γ 2CaO.SiO$_2$ (☐).
C.—Stable dolomite brick consisting of 3CaO.SiO$_2$ (⊙) and magnesia (M).

Fig. 1.—Photometer curves of Debye-Scherrer X-ray photographs.

or inadequate firing, while those which "dusted" (like an electric-furnace white falling slag) after use in the open-hearth furnace contained γ dicalcium silicate (see Fig. 1). This work emphasised the necessity of adjusting the chemical composition so that all the lime was combined but no unstable dicalcium silicate was present. It was therefore decided that the composition should be such that the principle constituents in the clinker were tricalcium silicate (3CaO. SiO$_2$) and magnesia, the reactions involved being essentially :—

6(CaO$_3$. MgCo$_3$) + 3MgO. 2SiO$_2$. 2H$_2$O $\longrightarrow$ +
    Dolomite   Serpentine
       2(3CaO. SiO$_2$)+ 9MgO + 2H$_2$O + 12CO$_2$.

Since the slight decrease in the serpentine addition below that theoretically required results in the presence of free lime, it is considered wise to keep slightly on the silica rich side of the 3CaO. SiO$_2$ composition. This may result in the presence in the clinker and fired brick of a little dicalcium silicate, and, hence, certain of the known stabilisers are added to the batch to prevent its inversion from the β to the γ form, a change that occurs below

675° C. with a disastrous increase in volume. X-ray examination of numerous samples made during the last few years confirms that the main products are, in fact, magnesia and tricalcium silicate, but that small amounts of β dicalcium silicate may also be present. The state of combination of the alumina and iron oxide has not been ascertained at all definitely, although it would seem likely that they occur either as glass or as brownmillerite ($4CaO. Fe_2O_3. Al_2O_3$).

One other reaction requires to be considered before the general principles involved can be understood, viz., the tendency of tricalcium silicate to break down at moderate temperatures—in particular round about 1200° C.—to give dicalcium silicate and free lime,[2]

$$3CAO. SiO_2 \longrightarrow 2CaO. SiO_2 + CaO.$$
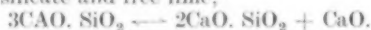
The reaction is generally sluggish, but as will be shown later, it can be troublesome in connection with the firing and subsequent storage of dolomite bricks.

The Production of Stabilised Dolomite Clinker

The batch used consists of high-grade raw dolomite, together with serpentine and small amounts of stabilisers. The materials are first wet ground in a tube mill, and then pass to a slurry tank where they are kept stirred until being fed into the top of a rotary kiln.

The firing zone of the kiln is lined with magnesite bricks, although special dolomite bricks have recently been used with marked success. The kiln is fired with pulverised coal and attains a temperature in excess of 1600° C. As the slurry passes through the kiln it first loses water, then carbon dioxide from the dolomite. From then onwards reactions occur which eventually lead to the formation of $3CaO. SiO_2$ and MgO. If the temperature in the firing zone is particularly high, the pea-size particles tend to grow and may even yield balls of clinker several inches in diameter. The red-hot clinker leaving the bottom of the kiln passes through a cooler and thence, via elevators, to the crushers. The crushed product is mechanically sieved and sieve fractions are stored in steel hoppers.

Manufacture of Stabilised Dolomite Bricks

The various grades of clinker obtained in this way are recombined by weighing out fixed quantities of the different grain-size fractions and conveying them to a mixer. The grading of the batch varies somewhat from plant to plant, but the following may be considered a typical range:—

Coarse	..	..	..	..	..	75 to 55%
Medium	..	..	..	..	..	15 to 5%
Fines	..	..	..	..	..	40 to 20%

The batch is moistened with about 4% of water, and weighed quantities are placed in the brick boxes of a hydraulic press. The moulding pressure used in generally between 10,000 and 15,000 lb. per sq. in.

The drying of dolomite bricks has given rise to a number of difficulties in spite of their low moisture content. The cause of these troubles is still rather obscure, but it is known that they can be minimised if the drying is done at as low a temperature as possible and in a stream of dry, clean air. If the drying conditions are not right, considerable cracking of the bricks may occur either in the drier or during subsequent kiln-firing.

The firing is carried out in down-draught kilns, either circular or rectangular, using coal, oil or producer gas as a fuel. The maximum temperature is 1400°–1450° C. If insufficient firing treatment is given, e.g., if a firing temperature of only 1300° C. is employed, some of the tricalcium silicate may break down in the manner already indicated and the product will then contain free lime. This may result in crumbling in storage. There is little doubt that some of the $3 CaO. SiO_2$ in the clinker breaks down however dolomite bricks are fired, but considerable evidence obtained in both laboratory and works tests show that any lime that may be formed in this way recombines during subsequent firing of the bricks at higher temperatures. A convenient indication of the firing treatment is afforded by the firing shrinkage, which is approximately $\frac{3}{16}$ in. on the 9 in. length of a standard square.

Manufacture of Special Dolomite Bricks

Semi-Stable Bricks.—Some of the earliest bricks to give useful service in steel-works (particularly in arc-furnace side walls) were of the semi-stable type. They contained large quantities of free lime, but could be stored long enough to make their use practicable and had a fairly good thermal-shock and slag resistance. Bricks of this type can be made by mixing " basic " with a flux or slag, moulding with a temporary bond, e.g., tar, and firing in the ordinary way. They are difficult to make and often difficult to store, but, as will be shown later, have a useful, if limited, application.

Dolomite-Magnesite Bricks.—It has been shown that the replacement of the intermediate fraction in a stabilised-dolomite brick by dead-burned magnesite results in an increase in thermal-shock resistance. Thus a spalling resistance index of 30 reversals[3] can sometimes be obtained in this way, as compared with one or two reversals for the normal stabilised brick. The manufacturing technique, apart from the change in batch composition, is similar to that of the ordinary brick.

Dolomite-Chrome Bricks.—A great deal of work has been done on dolomite bricks made with additions of chrome ore. The change is purely one of batch composition, the object being to increase the thermal-shock resistance.

Magnesite-Dolomite Bricks.—At the other extreme, magnesite bricks have been made in which 20% or 40% of the magnesite was replaced by stabilised-dolomite clinker. Here, again, the manufacturing conditions are similar to those of magnesite brick-making, apart from the change in batch composition.

Properties of Dolomite Bricks

Stabilised-Dolomite Bricks.—The general properties of two typical dolomite bricks and of the magnesite bricks which they replace are shown in Table I. A selected analysis of one such brick is as follows:—

Silica	..	..	..	14·44%	Lime	..	..	..	40·04%
Ferric oxide	..	..	3·44%	Magnesia	..	..	..	40·30%
Alumina	..	..	..	1·50%	Loss on ignition	..	0·25%

It will be seen that the porosity and permeability of such dolomite bricks are of the same order as those of the magnesite bricks, whilst they show equally good volume stability at 1500° C. Their cold crushing strength is high, as is also their refractoriness-under-load, whether determined by the rising-temperature or by the maintained-temperature test. The thermal-shock resistance is rarely greater than two reversals, whereas 5–8 reversals are more usual with magnesite bricks, while special bricks such as the M4 in Table I withstand 30 reversals without cracking.

TABLE I.

Code No.	Special Magnesite Brick M4	Ordinary Magnesite Brick M17	Typical Stabilised Dolomite Bricks X6	X7
Apparent porosity	24·2	18·7	22·1	24·7
Bulk density :				
G., per ml.	2·67	2·89	2·58	2·53
Lb. per cu. ft.	167	181	161	158
Apparent specific gravity	3·52	3·56	3·31	3·36
Cold crushing strength (9 × 4½ × 3 in. brick on end), lb. per sq. in. ..	7170	>8300	>8300	5090
Permeability to air (perpendicular 9 × 3 in. face, through 1 skin), C.g.s. units	0·08	0·12	0·088	0·12
After-Contraction (2 hr., 1500° C.), % ..	1·0	0·1	0·0	0·2
Refractoriness-under-load (maintained temperature test : 25 lb. per sq. in. at 1600° C.)	Failed in 11 mins.	Not determined	Failed in 32 mins.	Failed in 11 mins.
Rising temperature test (50 lb. per sq. in.), ° C.:				
Initial softening	—	1450	1540	1460
Rapid softening	—	1520	1610	1510
Fail	—	1540	1680	1600
Thermal shock resistance (No. of reversals required to produce failure)	>30	7	2	3

2 E. Carlson, *Journal of Research of the National Bureau of Standards*, 1931, 7, No. 5, p. 896.

3 The test methods used are those described by one of the authors (J. H. C.) in a recent article in *Iron Age*, 1941, **147**, p. 33 and p. 47.

In addition to the properties given in Table I, the following may be considered typical for the present-day stabilised-dolomite brick :—

Thermal expansion (20–1000° C.)	1·31%.
Thermal conductivity (1000° C. mean)..	15 B.th.u. (of magnesite, 25 B.th.u.)
Specific heat (750–20° C.)	0·25.
Hydration resistance	No crumbling after boiling in water for 24 hours.
Free lime	No free lime by the glycerol or White's test.

Other Types of Dolomite Bricks

Semi-Stable Bricks.—A selected analysis of one such brick is as follows :—

Silica	4·27%	Lime	51·66%
Ferric oxide ..	2·53%	Magnesia	38·21%
Alumina	2·16%	Loss on ignition ..	1·07%

It will be seen that the material does not differ greatly in analysis from the ordinary " basic " used for fettling open-hearth furnaces. The properties of samples of this type are summarised in Table II, column 1. It will be seen that, in addition to a comparatively low porosity and moderately good crushing strength, the brick has a fairly high refractoriness-under-load and an unusually good thermal-shock resistance. Furthermore, its resistance to slags high in iron oxide and lime is greater than that of the ordinary stabilised-dolomite brick. It has, however, one serious limitation, viz., it can be stored for only a limited period.

TABLE II.
PROPERTIES OF VARIOUS OTHER BRICKS CONTAINING DOLOMITE.

	1 Semi-Stable Dolomite Brick	2 80/20 Dolomite-Magnesite Brick (Special Grading)	3 80/20 Magnesite-Dolomite Brick	4 60/40 Magnesite Dolomite Brick
Porosity, %	22·8	26·4	19·2	20·4
Bulk density, G. per c.c.	2·52	2·50	2·79	2·72
Specific gravity (by porosity)	3·27	3·40	3·45	3·41
Crushing strength (9 × 4½ × 3 in. brick, on end), lb. per sq. in.	3680	4700	8740	7380
Permeability (perpendicular to 9 × 3 in. face, through 1 skin), C.g.s. units	0·29	0·36	0·121	0·097
After-contraction (2 hr., 1500° C.), % ..	1·2	0·7	0·2	0·7
Refractoriness-under-load (50 lb. per sq. in.), ° C.:				
Initial softening ..	1360	1430	1370	1400
Rapid softening ..	1520	1500	1510	1580
Fail	1610	1700	1650	1710
Refractoriness-under-load (25 lb. per sq. in., maintained at 1600° C.)	—	10% deformation after 49 min.	—	—
Thermal shock resistance (No. of reversals required to produce failure)	23	5	15 >26	13 } 15 16 }
Slag resistance (when tested with "4Fe₂O₃.CaO," slag at 1650° C.)	Definitely higher than stabilised-dolomite brick. No " bursting " expansion with iron oxide.	Similar to that of stabilised-dolomite brick. No " bursting " expansion.	Only slightly inferior to magnesite. Show volume stability at this temperature.	—

Dolomite-Magnesite Bricks.—A typical analysis of a specially graded brick in which the stabilised clinker was replaced in the intermediate section by magnesia is as follows :—

Silica	11·96%	Lime	31·40%
Ferric oxide	3·24%	Magnesia	51·60%
Alumina	1·60%	Loss on ignition ..	0·14%

The properties of this brick are summarised in Table II, column 2. The brick is similar in many respects to the stabilised-dolomite brick, but has a thermal-shock resistance of 5 reversals. Batches have been made of which the thermal-shock resistance was much higher, e.g., 15–30 reversals, but the problem of maintaining such values, both in brick-making and in use, is considerable. The specific heat of a brick of this type was found to be 0·25₅, while its thermal expansion (20–1000° C.) was 1·26%.

Dolomite-Chrome Bricks.—No description of these bricks will be given, although a considerable amount of laboratory test data are available. They possess one serious limitation, viz., the tendency of the chrome to react at the working temperature with the dolomite clinker, with the production of a great deal of " melt." This results in serious softening, which has so far prevented their commercial application in steel furnaces.

Magnesite-Dolomite Bricks.—Trial batches of magnesite bricks have been made in which 20% or 40% of the magnesite was replaced by stabilised-dolomite clinker. The properties of such bricks are summarised in Table II, columns 3 and 4. It will be seen that the samples examined had a low porosity, a high refractoriness-under-load and an unusually high thermal-shock resistance. Slag tests using a 4/1 mixture of iron oxide and lime (representing basic open-hearth furnace dust) showed that these bricks had a slag resistance only slightly inferior to that of magnesite itself. The change in slag resistance on passing from magnesite to dolomite brick is illustrated in Fig. 6, which shows the results of tests on laboratory-made samples.

Application to Steelworks Furnaces

The Open-Hearth Furnace.—The following extracts from Minutes of the Research Directing Committee of The United Steel Companies, Ltd., will serve to show that the dolomite brick, so extensively used to-day, only gained a foothold after competing with magnesite bricks *under pre-war conditions :—*

Date of Minute.

Dolomite Bricks with Addition of Sudanese Rock.

16/1/35. (*a*) A trial panel, 5 courses high (from the foreplate level), 23 in. long and 18 in. wide, built in the back wall of Stocksbridge (S. Fox & Co., Ltd.) H basic furnace slightly to the left of a position immediately over the tap-hole, after 14 weeks' service was found to have the following thickness remaining:—

	Dolomite Bricks with Sudanese Rock Addition	Adjacent Magnesite Bricks
Course 1	15 in. left	16 in. left
,, 2	14 in. ,,	14 in. ,,
,, 3	11 in. ,,	12 in. ,,
,, 4	10 in. ,,	9 in. ,,
,, 5	9 in. ,,	9 in. ,,

The above results would appear to warrant extended trials.

(*b*) One hundred and ninety-six dolomite bricks, tested in the back wall of K furnace at Templeborough, were found to have 1 in. less good surface than magnesite bricks in a similar position.

(*c*) The tap-hole of G furnace at Templeborough has just been lined on each side with a 3 ft. 6 in. patch of these bricks.

16/9/35. The trial patch in the lining of the tap-hole in G furnace at Templeborough still continues to function satisfactorily.

14/11/35. Upon cutting out the tap-hole of G furnace at Templeborough when down for repairs, the dolomite bricks were found to be in perfect condition and were put back again for a further run of about 26 weeks.

In this position, dolomite bricks are considered to be as good in every respect as magnesite bricks, which are much dearer.

1/4/36. The trial of standard dolomite bricks in the tap hole of G furnace at Templeborough has now been completed ; the bricks have been in service for 42 working weeks, during which 519 casts have been produced with an output of 41,765 tons.

The bricks are still in perfect condition, but some were damaged in taking them out. In this position Steel, Peech & Tozer consider these bricks to be fully equal to magnesite bricks.

8/11/37. Templeborough tap-hole trials.

After 28 weeks in D furnace the dolomite were generally as good as a magnesite brick tap-hole.

Equally satisfactory results were obtained in a later trial in G furnace despite the fact that, in the latter case, examination of the tap-hole revealed steel to be present between each layer of dolomite bricks.

As a result of the above trials and similar tests made at Appleby-Frodingham, dolomite bricks have been widely applied in the open hearth furnaces of The United Steel Companies, with a considerable saving in money in peace time, and with an even more important saving in shipping at the present time.

The positions in which they have been found to give satisfactory service are summarised in Table III and Fig. 2.

TABLE III.
DOLOMITE BRICKS IN OPEN-HEARTH FURNACE.
PRESENT STANDARD PRACTICE.

Position†	Type of Brick	Comments
7 Bath bottom.	Stabilised dolomite.	Replaces all magnesite bricks in fixed furnaces and top course in tilting furnaces.
8 Bridge bank. } 9 Banks. }	Stabilised-dolomite.	Complete replacement in fixed furnaces and partial replacement in tilting furnaces.
12 Back walls.	Semi-stable.	Life in fixed furnaces similar to chrome-magnesite bricks.
	Dolomite-magnesite.	Limited success in fixed furnaces.
	Magnesite-dolomite (80/20).	Trials in tilting furnaces gave life approx. equal to chrome-magnesite bricks.
	Magnesite-dolomite (60/40).	Trials in tilting furnaces suggest inferior to chrome-magnesite bricks.

† *Cf.* First Report on Refractory Materials, p. 212, *Iron and Steel Institute*, 1939, *Special Report No.* 26.

Bath Bottom, Banks and Bridge Banks.—The encouraging results obtained with stabilised-dolomite bricks in tap-holes has led to a gradual replacement of magnesite bricks in fixed-furnace hearths by dolomite bricks, until to-day the authors' company has no hesitation in building a new hearth without any magnesite bricks at all. With tilting furnaces working the hot-metal process the hearth is rarely seen, and hence it is not surprising that replacement has proceeded more gradually. It has, however, been found
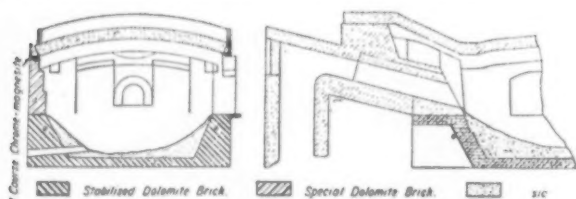

Fig. 2.—Main positions in basic open-hearth furnaces in which dolomite brick and basic are employed.

that stabilised-dolomite bricks can be used with fair success in the back banks where they can be seen and fettled, and, as a result, partial replacement of the hearth bricks has been tried. Thus, at one plant eight courses in the back wall around the furnace ends, four above and four below the sill, are used, the bricks extending for the full thickness of the lining. About 3000–4000 dolomite bricks are used for a normal repair in positions in which magnesite bricks were previously employed. In the front banks of tilting furnaces the use of dolomite bricks is more doubtful, since fettling is difficult.

The use of bricks in the sub-hearth is essentially an insurance against premature failure of the monolithic hearth, and hence, unless such failure actually occurs, the bricks are not subject to any real test. It will therefore be asked whether, in fact, break-outs have been more frequent when using dolomite bricks. Even if all other variables were controlled, a fair answer to this question could be given only after a long period of years. All that can be said at the moment is that, in the authors' experience, break-outs on furnaces having dolomite-brick hearths have actually been less in proportion to the number of hearths lined in this way than have been experienced with magnesite during the same period. In one case, where a break-out did occur through a sub-hearth consisting of dolomite bricks, the latter were critically examined in the laboratory. Chemical analysis showed that the iron-oxide content had increased in the top layers from about 3% to 17%, and there had been a corresponding drop in the magnesia content. The silica was only 8·6%, i.e., less than in the original brick, presumably owing to the diluting action of slags high in iron oxide and lime. This result, which falls in line with later studies on open-hearth furnace bottoms, suggests that dolomite bricks used in this position tend to become similar in composition and texture to the adjacent " basic." There is, therefore, no reason to believe that, if a hearth wears thin enough to expose the dolomite bricks, there will be any increase in the rate of wear. Indeed, at one steelworks, where the conditions had been particularly bad, it was stated that the dolomite bricks had stood up better than would have been expected of magnesite bricks.

Tests were also made on the " break-out " hearth to see whether prolonged heating at about 1200° C. had resulted in any dissociation of the tricalcium silicate. The bricks showed no crumbling on boiling in water for 24 hours, and there is no reason to believe that they were any less stable after use than magnesite bricks. Indeed, the percentage recoveries from used magnesite and dolomite hearths would appear to be of the same order.

Back Walls.—Attempts to use ordinary stabilised-dolomite bricks above the hearth level have mostly resulted in premature failure, owing to spalling. More recently, bricks have been produced, e.g., the dolomite-magnesite and semi-stable dolomite bricks mentioned earlier in this paper—that have given more encouraging results.

Thus, with the 80/20 type dolomite-magnesite brick, in which the magnesite is present in the intermediate section, back-wall trials in fixed furnaces showed a life of about 8 weeks, as compared with 11 weeks for chrome-magnesite bricks.

Still more encouraging results have been obtained with semi-stable bricks, which have recently given back-wall lives of the same order as chrome-magnesite bricks. These bricks still possess one serious limitation—they must be used within a short time—although attempts are now being made to overcome this by impregnating the fired brick with organic stabilisers.

With tilting furnaces the position is more difficult, because the slag runs up the back wall during tilting. Some success has been obtained with small trials of stabilised-dolomite bricks, and more recently results approximately equal to those given by chrome-magnesite bricks have been obtained in trials of the 80/20 magnesite-dolomite type. Trials of semi-stable bricks are in hand, but it is too early to state whether these will be successful. Good results have also been obtained with stabilised-dolomite bricks in the splays of tilting furnaces.

Considerable quantities of imported chrome and magnesite are also used for the parging of tilting furnaces. Preliminary trials, using finely ground stabilised clinker, suggest that a cement of this type may, with some development, provide an adequate substitute.

Reheating Furnaces.—Scale formation may be so serious in reheating furnaces working at 1200° C. and upwards that the use of firebrick hearths is precluded. In such hearths, the use of chrome-magnesite or magnesite bricks has been usual, but in the last few years, extensive use has been made of stabilised-dolomite bricks with complete success.

Cement.—Special cements have been developed for use with stabilised-dolomite bricks. They consist essentially of finely ground stabilised-dolomite clinker, and can be used either wet or dry. No special precautions, such as the use of oil-bonded cements, are necessary with stabilised-dolomite bricks. With bricks of the semi-stable type, however, dry-setting or a non-aqueous cement must be employed.

Ball and Roller Bearings

It has long been customary for users of bearings to consult the technical departments of bearing manufacturers during the design stage of their products, so that bearings could be recommended having regard both to their suitability for the duty and the possibility of early delivery. The importance of this preliminary action is now more apparent as the Bearing Panel of the Ministry of Supply have issued two schedules of War-Time Restrictions of Ranges of Anti-Friction Bearings. One of these deals with ball and parallel roller bearings, the other with tapered roller bearings.

The restriction in ranges of bearings by the Bearing Panel is definitely a move in the interests of all users, but in order that the greatest benefits can be secured it is especially desirable that all engineers using bearings should consult the technical departments of bearing manufacturers at an early stage in the design of the product.

Organic Reagents for the Quantitative Analysis of Iron and Steel

By E. C. Pigott

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The numerous organic reagents developed for the quantitative analysis of iron and steel are surveyed. Prepared with a view to bridging the gulf between present practice and academic achievement, the survey includes a summary of the introduction of these reagents as well as of their specific application.

GREATER familiarity with the known properties of the newer organic reagents would lead to wider adoption in the field of ferrous analysis. A vast amount of research has been expended by numerous investigators, and many of the published methods for iron and steel possess definite advantages. It was thought, therefore, that a more or less complete summary of the introduction of such reagents and of their specific application to the analysis of iron and steel would serve as a useful review and as a selective key to scattered information.

Gravimetric Reagents

Of the more recognised reagents, a few are of long-standing. α-*Nitroso-β-naphthol*, so extensively used for the precipitation of COBALT,[1] was first applied in 1885 by Ilinski and von Knorre[2] as a precipitant for iron. Application to the determination of cobalt in steel has been discussed by Eder[3] (1922) and Hoffman[4] (1932). For cobalt, the reagent is invariably applied to dilute hydrochloric acid solutions in order to effect a complete separation from nickel. The usual acid concentration of 1 : 20 is too pronounced for small amounts of the element and may safely be reduced to 1 : 50, a concentration more conducive to complete precipitation and at which the separation from nickel is still complete. Where the amount of cobalt is very small an acetic-acetate medium is necessary, though contamination may then occur.

In 1905, Tschugaeff[5] found the invaluable reaction of NICKEL with *dimethylglyoxime*, and this was soon applied to steel-analysis.[6, 7] In the separation of nickel from copper, cobalt or much manganese, an acetic-acetate medium is preferable since in ammoniacal solution, copper contaminates the nickel complex and cobalt causes the precipitation to be incomplete. In the presence of cobalt, ferric iron should be absent or contamination with $FeCoC_{12}H_{19}N_6O_6$ occurs ; reduction is conveniently effected by means of alkali sulphite. The nickel complex is appreciably soluble in solutions containing excessive amounts of acetic acid. The reaction as applied to small amounts of nickel in steel has been investigated.[8]

Cupferron, a very useful precipitant for IRON and several other constituents of steel, was proposed by Baudisch[9] in 1909. Direct applications to iron and steel include the determination of ZIRCONIUM, evolved by Lundell and Knowles[10] in 1920, and Cunningham's method[11] for TITANIUM (1933). The properties of cupferron (amino-nitroso-phenylhydroxylamine) are responsive to pH adjustment and have by no means been fully exploited. The present writer has found ALUMINIUM to be quantitatively precipitated from dilute formic acid solution.

The corresponding naphthyl compound (*neo-cupferron*), described by Baudisch[12] in 1937, is rather more sensitive, especially in the precipitation of COPPER from 3·5 N

hydrochloric acid. As the micro-chemical counterpart of cupferron, it serves for the precipitation of minute amounts of IRON without the need for a preliminary concentration.

Simple acid-oxidation methods fail to quantitatively precipitate TUNGSTEN when present in small amounts and treatment with an alkaloid becomes necessary. In 1895, Cremer[13] applied *cinchonine*.[14] *Benzidine* was proposed by von Knorre[15] in 1905, and his procedure has been discussed by Wdowiszewski.[16] Recently, benzidine has been used also for the estimation of PHOSPHORUS[17] and of COPPER[18, 19] in iron and steel.

The precipitation of MOLYBDENUM as a *cinchonine-thiocyanate* complex forms the main reaction in a reliable method evolved by Johnson[19a] for alloy steels.

Since Berg's introduction[20] of 8-*hydroxyquinoline* (oxine) 1926, over a hundred papers have appeared dealing with specific applications, yet only a few relate to ferrous analysis. As the result of developing a cyanide-reaction evolved by Heckzo,[21] the present writer[22] has devised simple conditions under which the reagent becomes virtually specific for ALUMINIUM in iron and steel. Other oxine methods for aluminium involve standard separations.[23-26] The reagent has also been applied to the determination of MOLYBDENUM[27] and BERYLLIUM[28] in ferrous metals, TITANIUM[29,30] in stainless steels, and ZIRCONIUM in ferro-zirconium.[30] *Dibromohydroxyquinoline* was proposed by Zan'ko and Bursuk for the precipitation of ALUMINIUM[31] in 1936, and of COPPER[32] in 1937.

Benzoin-oxime was originally announced by Feigl[33] in 1923 as a reagent for COPPER and the precipitation has been described by Kar,[34] but a far more important application is as an almost specific precipitant for MOLYBDENUM, a reaction investigated in 1932 by Knowles,[35] whose process has superseded older methods, especially for irons and steels containing vanadium. Silverman[36] has applied the process to ferro-molybdenum and Taylor-Austin[37] has described a method for cast-iron. As an alternative to ignition of the complex, Sterling and Spuhr[38] recommend conversion of the benzoin-oxime complex to lead molybdate and Furman and Flagg[39] have devised a volumetric treatment.

A recent and outstanding investigation is that of Schoeller and his collaborators into the separation of

1 Ilinski, *Chem. Ztg.*, **19**, 1421 (1895).
2 *Chem. Ztg.*, **18**, 2728 (1885).
3 *Chem. Ztg.*, **46**, 430 (1922).
4 *Bur. Stand. Research*, **8**, 659 (1932).
5 *Z. anorg. Chem.*, **46**, 144 (1905); *Ber.*, **38**, 2520 (1905).
6 Wdowiszewski, *Stahl und Eisen*, **28**, 960 (1908).
7 Prettner-Spandau. *Chem. Ztg.*, **33**, 396 (1909).
8 Jones. *Analyst*, **54**, 582 (1929).
9 *Chem. Ztg.*, **33**, 1298 (1909).
10 *Ind. Eng. Chem.*, **12**, 562 (1920).
11 *Ind. Eng. Chem.*, Anal. ed., **5**, 305 (1933).
12 Amer. Chem. Soc., Sept. meeting, 1937.

13 *J. Soc. Chem. Ind.* (1895), 679.
14 Hillebrand and Lundell. *Applied Inorg. Anal.*, 553 (1929).
15 *Ber.*, **38**, 783 (1905).
16 *Z. anal. Chem.*, **87**, 36-8 (1931).
17 Pil'nik. *Stal*, **6**, No. 9, 74 (1936).
18 Spacu and Macarovici. *Chem. Zentr.* (1937), II, 3784.
19 Mukhina. *Zavod Lab.*, **4**, 150 (1935).
19a *Iron Age*, **132**, No. 2, 16 (1933).
20 *J. pr. Chem.*, **115**, 178 (1927).
21 *Chem. Ztg.*, **58**, 1032 (1934).
22 Pigott. *J. Soc. Chem. Ind.*, **58**, 139 (1939).
23 Bright and Fowler. *J. Res. Nat. Bur. Stand.*, **10**, 327 (1933).
24 Gadeau. *Rev. Met.*, **32**, 398 (1935).
25 Taylor-Austin. *Analyst*, **63**, 566-92 (1938).
26 Mukhina. *Zavod Lab.*, **5**, 715 (1936).
27 Mukhina. *Zavod Lab.*, **3**, 1075 (1935).
28 Berg and Teitelbaum. *Z. anal. Chem.*, **81**, 1 (1930).
29 Arend, *Z. anal. Chem.*, **89**, 96 (1932); *Arch. Eisenhüttenw.*, **4**, 265 (1930).
30 Trinberg. *Zavod Lab.*, **4**, 735-8 (1935).
31 *J. App. Chem.*, U.S.S.R., **9**, 895 (1936).
32 *Zavod Lab.*, **6**, 675 (1937).
33 *Ber.*, **56** (B.), 2083 (1923).
34 *Ind. Eng. Chem.*, Anal. ed., **7**, 193 (1935).
35 *Bur. Stand. Research*, **9** (1932).
36 *Ind. Eng. Chem.*, Anal. ed., **12**, 343 (1940).
37 *Analyst*, **62**, 107 (1937).
38 *Ind. Eng. Chem.*, Anal. ed., **12**, 33 (1940).
39 *Ind. Eng. Chem.*, Anal. ed., **12**, 738 (1940).

COLUMBIUM from TANTALUM, resulting in the application of *tannic acid*.[40, 41]

The determination of ZIRCONIUM in special steels and in ferro-zirconium has been greatly simplified by the application of *phenylarsonic acid*[42] (1933), *benzenearsonic acid*[42] (1933), *disodium methylarsenate*[43] (1937), *p-hydroxyphenylarsonic acid*[44] (1938) and *n-propylarsonic acid*[45] (1937), the latter being almost specific, even in the presence of titanium. By means of these reagents, amounts smaller even than 1 mg. may be readily separated. *p*-Hydroxyphenylarsonic acid serves also for the estimation of TITANIUM.[44]

Both SELENIUM and TELLURIUM are now used in special steels and precipitation may be very satisfactorily effected with the aid of *hydroxylamine hydrochloride*.[46]

Phenylthiohydantoic acid, proposed by Willard and Hall[47] in 1922 serves for the separation of COBALT from many elements but not from nickel or iron.

When applied to ammoniacal-citrate solutions, *α-benzil-dioxime* becomes a specific precipitant for NICKEL. The reaction was first described by Atack[48] in 1913.

Pyridine has been used in steel analysis by Mukhina[49] (1935) for the estimation of IRON, CHROMIUM, COBALT, NICKEL, COPPER AND ZINC. More recently, Spacu[50] has also discussed certain of these reactions, in which the elements are precipitated as pyridine-thiocyanate complexes (e.g., $Co(CNS)_2.4C_5H_5N$).

Colorimetric Reagents

Absolute measurement of colour intensity, afforded by the photoelectric absorptiometer, has given considerable impetus to the development of colorimetric methods. Within various ranges of ionic concentrations, most coloured compounds are reasonably stable to the actinic rays and the advantages of the absorptiometer have led to the determination of these permissible ranges.

In the ferrous field, organic colorimetry had its inception as early as 1838, when Piria applied *salicylic acid*[51, 52, 53] to the estimation of small amounts of IRON itself. *Thioglycollic acid* (mercaptoacetic acid),[54, 55] introduced in 1879, was suggested by Lyons[56] in 1927 as a particularly useful reagent for traces of IRON[57]; the sensitivity is one part in ten million. The acid is a colourless liquid, which in ammoniacal solution, reduces ferric iron to form an intensely purple divalent salt; manganese, nickel, cobalt, chromium, and uranium interfere. A useful reagent for FERROUS IRON is *αα'-dipyridyl*.[58, 59] A sensitivity of one part in five million is claimed for the reaction of FERRIC IRON with *7-iodo-8-hydroxyquinoline-5-sulphonic acid*,[60, 62] employed as a 0·2% aqueous solution at pH3.

In the delicate reaction of *diphenyl-carbazide* with the CHROMATE ion,[63] described by Cazeneuve[64] in 1900, the practice of employing a large excess of sulphuric acid is not to be recommended since the interference of vanadates, which furnish a similar colour, thereby becomes more marked. Large amounts of molybdate also interfere with the reaction. A photometric method for steel has been described by Koch[65] (1939). In 1913, Garratt[66] successfully

applied *disodium-1, 8-dihydroxynaphthalene-3-6 disulphonate* to the determination of small amounts of CHROMIUM in steel.

Much attention has been directed to the colorimetric estimation of ALUMINIUM, but the reagents proposed entail numerous preliminary separations and the pH-latitude is very limited. *Ammonium auric tricarboxylate* (aluminon), first applied by Hammett & Sottery[67] in 1925, is preferable to *alizarin S*, suggested by Atack[68] in 1915, to *quinalizarin*[69] (Kolthoff, 1927), and to *eriochrome-cyanine*[70] (Alten, 1934). Koch[71] (1939) has described a photometric method for steel using the latter reagent at pH6; iron, nickel, chromium and manganese are first removed by the mercury cathode. Quinalizarin is applicable also to the estimation of BORON in steel, and a method has been described by Kar[72] who also discusses the reaction of *curcumin* with the element.

Probably the most satisfactory colorimetric reagent for small amounts of COPPER is *sodium diethyldithiocarbamate* introduced by Delepine[73] in 1908; the copper reaction was introduced by Callan & Henderson[74] in 1929, and its application to mild steel was described by Hoar[75] in 1937. This sensitive reagent furnishes a brown coloration in alkaline solutions and the complex may be extracted with organic solvents; ferrous iron, aluminium, tin and zinc interfere. The useful *rubeanic acid* reaction with COPPER was found in 1926 by Ráy and Ray.[76] A photometric method for COPPER in cast-iron involves the use of *quinaldinic acid*.[77]

Colorimetric methods for NICKEL based on the *dimethyl-glyoxime* reaction have been described by Rollett[78] (1926), Deichman[79] (1935), Dietrich and Schmitt[80] (1938), and Murray and Ashley[81] (1938); iron may be kept in solution by means of citric acid but interfering colorations are produced by copper and cobalt. In the presence of an oxidising agent such as bromine-water, hypobromite, or hypochlorite, the sensitivity of dimethylgloxime is considerably increased and the oxidised complex is readily soluble.

Strychnin was found by Gregory[82] in 1909 to form a violet coloration with VANADIUM in concentrated sulphuric acid; titanium, molybdenum and tungsten do not interfere and Pickard[83] (1913) applied the reaction to steel. Another reagent more selective than hydrogen peroxide is *dihydroxymaleic acid*, applied by Mellor[84] in 1913 to the estimation of TITANIUM; no interference is caused by vanadium.

In 1918, Meaurio[85] found that *diphenylamine* serves as a reagent for VANADIUM, with which a violet coloration is furnished; titanium does not interfere.

Klinger and Koch[86] have devised a photometric method for TITANIUM by applying the *chromatropic acid* reaction with which columbium and tantalum do not interfere.

Thymol was applied to the determination of TITANIUM by Lehner & Crawford[87] in 1913; tungsten, molybdenum and chromium form interfering colorations and a high degree of acidity is required.

In 1938, Veinberg[88] introduced the extremely sensitive thymol-hypobromite reaction for NITROGEN in steel. *Nitroso-R salt*,[89, 90] a naphthol compound introduced by

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van Klooster in 1921, produces with traces of COBALT in alkaline solution, a deep red coloration, unaffected by acidification ; tin and titanium interfere. Ditz (1922) described a specific reaction for COBALT, provided by *acetone*[91] and ammonium thiocyanate.

The reaction of *β-nitroso—α-naphthol* with COBALT is the basis of a photometric method for steel proposed by Yoe and Barton[92] (1940).

Of the numerous colorimetric methods available for PHOSPHORUS, those based on the formation of the phospho-compound of molybdenum blue are outstanding since the interference of arsenic, ferric iron and nitrates may be overcome by the simple expedient of heating with alkali bisulphite. In the formation of the blue complex[93] alternative reductants to stannous chloride include *hydroquinone*[94] *p-methylaminophenol* ("elon")[95] and 1, 2, *4-aminonaphthol-sulphonic acid*.[96] A nephelometric method for PHOSPHORUS in steel is based on the reaction with *strychnine molybdate*.[97,99]

A photometric method for ARSENIC in steel[100] has been described by Rodden (1940). The distillate obtained from treatment with halogen acids and hydrazine sulphate, hypobromic acid and hydrochloric acid, is treated with ammonium molybdate and *hydrazine sulphate* to yield the arseno-compound of molybdenum blue.

In a photometric method for TUNGSTEN in steel,[101] evolved by Bogatzki (1938), *hydroquinone* is employed to furnish a red complex.

Indicators

The majority of internal organic indicators are of recent application.

Diphenylcarbazide was found by Agnew[102] in 1931 to be a most satisfactory indicator for CHROMIUM titrations.

91 *Chem. Ztg.*, **46**, 121 (1922).
92 *Ind. Eng. Chem.*, Anal. ed., **12**, 409, 19 (1940).
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94 Dell and Doisy. *J. Biol. Chem.*, **44**, 55 (1920).
95 Luizen. *Analyst*, **58**, 755 (1933).
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98 Clarke. *Analyst*, **56**, 518 (1931).
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102 *Analyst*, **56**, 24 (1931).

Willard and Young applied *diphenylamine sulphonic acid* and *diphenylbenzidine* to VANADIUM titrations[103] (1932). *oxidised sodium diphenylamine sulphonate*[104] to VANADIUM and CHROMIUM (1933), and *ortho-phenanthroline*[105] to CHROMIUM (1934). Poolish and Sullivan (1939) have also described the use of the latter indicator for CHROMIUM.[106]

In 1940, Wado and Isii[107] found *bromo-creosol blue* more satisfactory than *sodium alizarine sulphonate*[108] proposed by Cunningham and Hamner (1939) as an indicator in the acid titration of ammonia for NITROGEN in steel. *Methylene blue* was recommended for this titration by Kovtun[109] in 1937.

For the titration of quadrivalent VANADIUM, Andrev[110] in 1938, described the application of *fushin red* and *trypan red* which preclude difficulties arising from ordinary indicators, which form leuco compounds. *n-Phenylanthranilic acid* proposed by Kirsanov and Cherkasov[111] has been applied by Suitokomskii and Stepin[112] (1936) to VANADIUM, CHROMIUM and IRON titrations.

Alekseeva and Andronikov (1938) have described the use of *brucine* as an indicator for IRON.[113]

103 *Ind. Eng. Chem.*, Anal. ed., **4**, 187 (1932).
104 *Ind. Eng. Chem.*, Anal. ed., **5**, 154, 158 (1933).
105 *Ind. Eng. Chem.*, Anal. ed., **6**, 48 (1934).
106 *Iron Age*, **143**, 38 (1939).
107 *Sci. papers Inst. Phys. Chem. Res.* (Tokyo), **37**, 65 (1940).
108 *Ind. Eng. Chem.*, Anal. ed., **11**, 303 (1939).
109 *Zavod Lab.*, **6**, 229 (1937).
110 *Zavod Lab.*, **7**, 258 (1938).
111 *Zavod Lab.*, **5**, 143 (1936) ; *Bull. Soc. Chim.* [5], **3**, 817 (1936).
112 *Zavod Lab.*, **5**, 144, 263 (1936).
113 *J. App. Chem.*, U.S.S.R., **11**, 1024 (1938).
General and specific phases of the subject are dealt with in the following publications :
In *Organic Reagents for Metals* (Hopkin and Williams, 1938) and *The B.D.H. Book of Organic Reagents* (1941) many applications are described. A monograph by N. Strafford (*The Detection and Determination of Small Amounts of Inorganic Substances by Colorimetric Methods* ; Institute of Chemistry) contains procedures for certain constituents of iron and steel.
The application of the photoelectric absorptiometer to ferrous and non-ferrous analysis is described in detail by E. J. Vaughan in *Modern Methods in Metallurgical Analysis by means of the Spekker Absorptiometer* (Institute of Chemistry monograph, 1941).
A few organic reagents are used in methods devised for the Pulfrich Photometer (*Absolute Colorimetric Analysis of Metals* ; Zeiss, 1939).
The tintometric determination of chromium, copper, iron and aluminium by means of organic reagents is included in E. Taylor-Austin's contribution, "The Application of Colorimetric Methods to Metallurgical Analysis," *J. Soc. Chem. Indus.*, **60**, 29-39 (1941).
Two comprehensive text-books on colorimetric analysis are those by Snell and Snell (*Colorimetric Methods of Analysis* [Chapman and Hall (1936), Vo. I] and J. H. Yoe (*Photometric Chemical Analysis*, Vol. I, Colorimetry, and Vol. II, Nephelometry ; Wiley, 1928-9).

A Note on the Theory of Quenching[*]

By J. H. Awbery, B.A., B.Sc.

The heat transfer to a fluid from the plane surface of a solid has been studied. If the temperature of the surface of the solid is sufficiently far above the boiling point of the fluid, there is a regime in which a sheath of vapour forms between the solid and the fluid. It is shown that, during this regime, the heat loss H per unit area per second is $B(T_B - T_0)^{\frac{3}{4}}(k_i^2 agc/v)^{\frac{1}{4}}$, when B is a constant, approximately $0 \cdot 0015$ if thermal quantities are measured in calories.

A GOOD deal of experimental work has been carried out in recent years on the processes by which the heat is transferred from a heated object to a liquid in which it is immersed. Three regimes have been distinguished :—

(1) If the body is sufficiently hot, there is first a period during which the body of the liquid is separated from the solid by a vapour film ; the thermal conductivity of vapour is usually low, but the initially large temperature gradient results usually in the heat transfer being fairly considerable during this period.

(2) When the solid is cool enough and the film has become very thin, it breaks up so that over parts of the area the liquid and solid are in contact and at other parts bubbles form ; by becoming detached, they carry off heat from the surface by a process of mass transfer. The heat transmission coefficient in this period is usually greater than during the film regime.

(3) When the solid is definitely below the boiling point of the fluid, so that neither film nor bubbles can form, the process is the normal one of pure convection, and the transmission coefficient is much smaller than in the first two regimes.

The third regime has been very thoroughly studied, at least as regards heat loss from cylinders, but the laws of the heat flow during the first and second are not yet fully established, and there is no information as to the exact factors governing the temperature of transition between them. In the present note attention is confined to the first, or film, regime.

Approximate Theory of Heat Transfer in the Film Regime

Since our aim is to elucidate the processes occurring, it is preferable to take a highly simplified case, *viz.*, one in

which the cooling solid is a thin uniform plate lying horizontally with the liquid above it. The film will be assumed to be of uniform thickness h (which will, however, vary with time).

In this simplified case, it is clear that the pressure throughout the vapour is uniform and equal to that required to support the weight of the liquid. Whilst the regime lasts, therefore, the pressure will not vary with time, and, if the weight of the liquid is neglected, will be equal to the atmospheric pressure. But this pressure must of necessity be the vapour pressure of the liquid at the temperature of its own surface, since otherwise more vapour would be formed, or all would condense. Hence the temperature at the liquid-vapour boundary must be the boiling point (T_B) at the pressure prevailing, i.e., to our approximation, at atmospheric pressure. The solid will be assumed to be so thin that the temperature gradient within it may be neglected, so that its surface temperature, T_s, is also its mean temperature.[1]

The heat leaving unit area of the solid in time dt is $\cdot H dt$, where H is the heat transfer per unit area per sec. for a surface at temperature T_s, and this heat will travel across the vapour by radiation and conduction (since we shall give reasons later for supposing that the film is too thin for convection to occur). Assuming the vapour to be transparent to the radiation, the latter will not affect the temperature of the film, which will thus vary linearly with distance z from the solid-vapour boundary. In fact the temperature of the vapour is :—

$$T_v = T_s - \frac{z}{h}(T_s - T_B) = T_s\left(1 - \frac{z}{h}\right) + \frac{zT_B}{h}$$

Equating the heat lost by the solid to that travelling by radiation and conduction we have :—

$$H = E\sigma(T_s^4 - T_B^4) + \frac{k_v(T_s - T_B)}{h} \quad . \quad . \quad . \quad (1)$$

where E is the thermal emissivity of the solid, σ is Stefan's constant, k_v is the thermal conductivity of the vapour, and temperatures are understood to be measured on the absolute scale. In the case contemplated, $H = - W dT_s/dt$, where W is the heat capacity per unit area of the plate, and equation (1) is equivalent to :—

$$-\frac{W dT_s}{dt} = E\sigma(T_s^4 - T_B^4) + \frac{k_v(T_s - T_B)}{h} \quad . \quad (1a)$$

The heat reaching the liquid differs from that leaving the solid, since it includes also the latent heat of any vapour which condenses, viz., $-L\frac{dm}{dt}$, where m is the mass of vapour per unit area of surface, so that the heat reaching the unit area of the liquid per second is :—

$$E\sigma(T_s^4 - T_B^4) + k_v\frac{(T_s - T_B)}{h} - L\frac{dm}{dt} \quad . \quad . \quad (2)$$

We note, however, that provided there is sufficient liquid, this quantity must remain constant throughout the duration of the film regime, since the heat thus received at the surface of the liquid is carried away, by convection and otherwise, from a surface at constant temperature (the boiling point) to a mass of liquid at constant temperature with unchanging boundary conditions. An accurate expression for this flow is not available, but the results given by Fishenden and Saunders[2] suggest that the expression $Hd/k_l\theta = A(ag\theta d^3c/k_l\nu)^n$ gives a reasonable approximation for a cylindrical surface. Here H is the heat flow per unit area per unit time, d the diameter of the cylinder, k_l the thermal conductivity of the liquid, θ the temperature excess (in the present case $T_B - T_0$, where T_0 is the temperature of the fluid at a distance from the surface), c the specific heat of the liquid per unit volume, a its coefficient of expansion and ν its viscosity; g is "gravity" and n a constant.

1 An alphabetical list of symbols is given at the end of the paper.
2 "The Calculation of Heat Transmission," p. 172. London, 1932: H.M. Stationery Office.

Thus :

$$H = Ak_l^{1-n}\theta^1 + {}^n a^n g^n d^{3n-1}c^n\nu^{-n}$$

and since for sufficiently large cylinders the heat loss per unit area tends to become independent of the diameter, we may assume that in the limit, when the diameter increases indefinitely and the cylinder becomes a plane, then $3n - 1 = 0$ or $n = \frac{1}{3}$, a result which may also be obtained by considering the dimensions directly.

We thus take for a plane surface the expression :—

$$H = Ak_l^{\frac{2}{3}}\theta^{\frac{4}{3}}a^{\frac{1}{3}}g^{\frac{1}{3}}c^{\frac{1}{3}}\nu^{\frac{1}{3}}, \text{ i.e., } A\theta (k_l^2 agc/\nu)^{\frac{1}{3}}.$$

This is to be equated to expression (2), leading to the equation :—

$$aE(T_s^4 - T_B^4) + k_v\frac{(T_s - T_B)}{h} - L\frac{dm}{dt} =$$
$$A(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad (3)$$

From equations (1) and (3) we eliminate h and m $\left(= \int_0^h \rho dz\right)$ by means of the gas law. From the general equation for a perfect gas ($pV = RT$) it follows that $p = \rho RT/M$, where ρ is the density and M the molecular weight. Now, in the film, $T = T_s - z(T_s - T_B)/h$, and p is constant and approximately equal to 1 atm. Thus :—

$$\rho = \frac{Mph}{R[hT_s - z(T_s - T_B)]}$$

and

$$\int_0^h pdz = \frac{Mph}{R}\int_0^h \frac{dz}{hT_s - z(T_s - T_B)} = \frac{-Mph}{R(T_s - T_B)}\log$$
$$\left[hT_s - z(T_s - T_B)\right]_0^h$$
$$= \frac{-Mph}{R(T_s - T_B)}\log\frac{T_B}{T_s} = \frac{Mph}{R(T_s - T_B)}\log\frac{T_s}{T_B}.$$

Thus :—

$$m = \frac{Mph}{R(T_s - T_B)}\log\frac{T_s}{T_B} \quad . \quad . \quad . \quad (4)$$

By comparison of equations (1a) and (3) we have :—

$$-\frac{W dT_s}{dt} - L\frac{dm}{dt} = A(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} \quad . \quad (3a)$$

which may be integrated with respect to t, giving :—

$$WT_s + Lm + At(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} = B \quad . \quad (5)$$

Substituting for m from equation (4) this becomes :—

$$WT_s + \frac{LMph}{R(T_s - T_B)}\log\frac{T_s}{T_B} + At(T_B -$$
$$T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} = B \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and finally, eliminating h between equations (1a) and (6), we find :—

$$WT_s - \frac{LMpk_v\log(T_s/T_B)}{R\left[\dfrac{W dT_s}{dt} + E\sigma(T_s^4 - T_B^4)\right]}$$
$$+ At(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} = B \quad . \quad . \quad . \quad . \quad (7)$$

This, on the assumption made, is the accurate differential equation giving the relation between T_s, the temperature of the solid which is being cooled, and the time t. The constants A and B are independent of the particular fluid. B might be expressed in terms of the initial (or final) conditions. Thus, if the curve of temperature against time is extrapolated to a time t_0 at which the film is of zero thickness, so that $m = 0$ and $T_s = T_B$, equation (5) shows that :—

$$B = WT_B + At_0(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}}$$

and equation (7) becomes :—

$$W(T_s - T_B) - \frac{Lmpk_v\log(T_s/T_B)}{R[W dT_s/dt + E\sigma(T_s^4 - T_B^4)]}$$
$$+ A(t - t_0)(T_B - T_0)^{\frac{4}{3}}(k_l^2 agc/\nu)^{\frac{1}{3}} = 0 \quad (8)$$

In practice, of course, the film regime would have given place to the second regime before this condition was reached, but the extrapolation, serving to express the slope of the observed straightline relation, appears to be legitimate.

Solution of the Equations to a First Approximation

It does not appear possible to integrate the differential equation (8) in finite terms. A good deal of information may, however, be obtained from an examination of the experimental results of Speith and Lange,[3] who studied the time-temperature curve when a silver ball was quenched from about 800° C. in water at different temperatures. Thus H in this case is $- W dT_s/dt$. In common with practically all workers, they found an almost exactly linear relation between time and temperature during the film regime, and from the curves it appears that dT_s/dt is 26·0, 15·6 and 12·0° C. per sec. for cooling by water at 20°, 40° and 60° C., respectively. Thus in equation (1) of the present paper, W, dT_s/dt (and hence H), σ, T_s at time t, T_B (= 100° C.) and k_v are known. The last-mentioned quantity was estimated, at the high temperatures required, by means of Sutherland's equation with constants adjusted to fit the conductivities at the two temperatures for which values are given in International Critical Tables. There are thus two unknown quantities, E the thermal emissivity of silver, and h the thickness of the film. Numerical values were inserted in the equation and h was calculated, first assuming E = 1 (the highest possible value) and then E = 0·05 (the lowest likely value). The results are shown in Table I, and it should be noted that the calculation also shows that the two terms on the right of equation (1) are of comparable magnitude.

TABLE I.—COMPUTED THICKNESS OF VAPOUR FILM. (CM.)

Condition.	Water Temperature. ° C.					
	20°.	40°.	60°.	20°.	40°.	60°.
	Assuming E = 1.			*Assuming* E = 0·05.		
Initial	0·0180	0·040	0·053	0·026	0·090	0·194
At end of linear regime ..	0·0042	0·0046	0·0049	0·0044	0·0047	0·0051

Values of the same order were obtained for the film thickness by a similar analysis of some unpublished figures by T. F. Russell, in which the quenching fluids were organic materials of high boiling point. Taken together they seem to show that, under the conditions of such experiments, the vapour film is so thin that convection cannot occur, and they thus substantiate the statement made earlier in this paper.

Equation (6) was next applied to Speith and Lange's data. For the six conditions dealt with before, i.e., the beginning and end of the linear portion of the curves for water at 20°, 40° and 60° C., the values of WT_s vary from $1·35 \times 10^9$ to $2·74 \times 10^9$ dynamical units, whereas the second term $\frac{LMph}{R(T_s - T_B)} \log \frac{T_s}{T_B}$ varies from $0·000043 \times 10^9$ to $0·00145 \times 10^9$, even if the maximum possible value of h is taken.

It thus appears that the second term of equation (6) may be neglected in comparison with the others, and we thus obtain an immediate theoretical explanation of the widely observed fact that the time-temperature curves are approximately linear.

Moreover, the experimental results may now be used to deduce values of A and B. All the quantities in the modified equation (6), including t, the time, are known (k_i, c and v were taken from Kaye and Laby's Tables, at the appropriate temperatures) and hence the initial and final points of each curve give a pair of equations from which A and B may be calculated. The results are shown

3 *Mitteilungen aus dem Kaiser-Wilhelm-Institut für Eisenforschung*, 1935, **17**, 167.

in Table II, in the units which apply if thermal quantities are measured in calories.

TABLE II.—VALUES OF CONSTANTS A AND B.

	Water Temperatures. ° C.			Mean.
	20°.	40°.	60°.	
A	0·00178	0·00138	0·00140	0·0015
B	65·4	65·7	65·8	65·6

The constancy of B leaves nothing to be desired. As regards A, which depends directly on the slope of the time-temperature curve, there are deviations of over 10%, but there does not appear to be a systematic trend in the values; since they are deduced from slopes which vary more than two-fold, the agreement is not unsatisfactory, particularly when it is remembered that the results apply to a ball 2 cm. in dia., and the theory to a flat plate.

The outcome of this section is to show that, at least for conditions similar to those in silver-ball tests with water, equation (6) reduces to :—

$$WT_s + At(T_B - T_0)^{\frac{3}{4}}(k_i^2 agc/v)^{\frac{1}{4}} = B,$$

or expressing B in terms of the final state and inserting the numerical value of A,

$$T_s = T_B - 0·0015(T_B - T_0)^{\frac{3}{4}}(k_i^2 agc/v)^{\frac{1}{4}}(t - t_0)/W \quad (9)$$

Alternatively we may express B in terms of the initial conditions. If $T_s = T_s'$, when $t = 0$, the equation becomes :—

$$T_s = T_s' - 0·0015(T_B - T_0)^{\frac{3}{4}}(k_i^2 agc/v)^{\frac{1}{4}}t/W \quad . \quad (9a)$$

In either form this is a first approximation to the time-temperature curve, and in it temperatures are measured in ° C., time in seconds, the physical constants in calorie units, W in cal. per 1° C. per sq. cm. The numerical values taken in determining the constant A were those appertaining to a temperature mid-way between T_0, the temperature of the bulk of the fluid, and T_B, the boiling point to which it is supposed the boundary rises. They were determined from experiments on spheres instead of flat plates, so that the actual numerical value of A may need revision when data for flat plates become available

Conclusion

The equations so far deduced are expressed in a form appropriate for a thin plate, of which the surface and mean temperatures are indistinguishable. If, however, equations (9) or (9a) are differentiated with respect to time, we have :—

$$W\frac{dT_s}{dt} = - 0·0015(T_B - T_0)^{\frac{3}{4}}(k_i^2 agc/v)^{\frac{1}{4}} \quad . \quad . \quad (10)$$

In this form, the equation gives the heat loss per second per unit area from a flat body, and must be equally applicable to a massive one, in which T_s moves only slowly (the heat flow being adjusted by alteration of the temperature gradient within the body), as to a thin one (in which the heat loss results in a cooling of the whole), since the heat loss from a body of which the surface temperature is T_s cannot depend on conditions interior to that surface.

ALPHABETICAL LIST OF SYMBOLS USED.

A	a constant.	R	the gas constant.
α	coefficient of expansion of liquid.	σ	Stefan's radiation constant.
B	a constant (approx. 0·0015).	t	time.
c	specific heat of liquid.	t_0	time at which $h = 0$.
d	diameter of cylinder.	T	temperature.
E	thermal emissivity of solid.	T_0	temperature of bulk of liquid.
g	acceleration due to gravity.	T_B	boiling point of liquid.
h	thickness of vapour film.	T_s	surface temperature.
H	heat loss per unit area per second.	T_s'	initial value of T_s.
k_l	thermal conductivity of liquid.	T_v	temperature of vapour.
k_v	thermal conductivity of vapour.	T'	mean between T_0 and T_v.
L	latent heat of vaporisation of liquid.	θ	temperature difference between solid and liquid.
m	mass of vapour per unit area.	V	volume per gramme-molecule of vapour.
M	molecular weight of fluid.		
v	kinematic viscosity of liquid.	W	heat capacity of solid per unit area.
n	a constant (approx. ½).		
p	pressure of vapour.	z	distance within fluid from solid boundary.
ρ	density of vapour.		

The Chrome-Hardening of Cylinder Bores

Some data are given on the wear-resisting properties of chromium-plated cylinder bores. Methods of application of chromium are reviewed, and attention is directed to the proper bonding of the chromium to the base metal. It is noteworthy that a porous coating to the cylinder bore is superior to a bright, dense coating, because it holds the lubricating oil. Difficulties still to be overcome in the application of the process are concerned mainly with engineering problems.

THE problem of cylinder and piston wear has been exercising the minds of manufacturers and users for many years. Considerable attention has been given to the development of suitable methods of finishing cylinder bores, also in machining operations prior to finishing, with the result that cylinder life generally has been lengthened. The subject of cylinder wear obviously cannot be divorced from pistons, rings, cylinder liners and lubricants, and manufacturers and lubricant producers have contributed in no small degree to increase the life of cylinders in service. Not long ago cylinder material was considered to be the outstanding factor as regards life, and wear was thought to be in direct ratio to the hardness of the materials used. To-day, the question of hardness arises chiefly in comparing similar castings and not in connection with their wear resistance. But wear of some of the most important parts of the engine, such as cylinders, rings, crankshafts, and ring grooves, continues to be a topic of keen interest to engineers, particularly when the output of engines of a certain size and weight is stepped up from time to time.

Considerable progress has been made in reducing wear of cylinders, piston-rings, and piston-ring grooves, by means of the chrome-hardening process, and the results of many tests emphasise the advantages this process offers. Recent data on the subject are given by Van der Horst,[1] who also reviews the way in which the application of chromium metal on the cylinder bore affects lubrication and choice of fuel. He further deals with the method of application—that is, proper bonding to the base material, and the properties of chromium metal as they are good or bad for this purpose.

Cases of Cylinder Wear

The causes of cylinder wear have been the subject of many disputes, and considerable research work has been done to determine how much corrosion, abrasive matter, lubrication conditions, overloading the engine, idling the engine, bad combustion, overcooling, overheating, the choice of fuel, of lubricating oil, engine design, and other factors cause wear, and to what extent such factors do so. Some of the possibilities mentioned only lead up to others ; overcooling will lead to corrosion, poor combustion to both corrosion and carbonisation. Some experienced engineers assert that corrosion is the only factor of wear. But in such cases, what is to be said of engines that run under conditions where sand dust or other dust can hardly be removed by filtering ? Certainly, such engines wear very badly, and one would assume that such wear is of an abrasive character.

Suspended matter, in the fuel or in the air, such as sand or dirt of any kind, naturally affects the wear on cylinders. Thus careful filtering of the fuel is extremely important in Diesel engines to prevent trouble with the pumps ; but effective filters will take care of this difficulty. Under certain conditions, especially when the engines operate in dust-laden air, filtering the air becomes necessary.

Another factor that can affect wear is suspended water, particularly salt water, if as much as 1 to 5% is present. Water can be taken in either by the air or the fuel ; but under the usual specifications for fuel, the amount of water is too small to influence wear, especially in comparison with the amount of water which is taken in with air and generated by combustion. However, water is more likely to be introduced when water-cooled pistons are used, because then there is the possibility of leakage. The action of suspended water on the cylinders must be considered as corrosive.

The sulphur content of fuel does not become an important factor in wear until it reaches 1%, but once it exceeds 2% its effect becomes distinctly noticeable. This action must also be considered as corrosion. Even in such cases, however, exceptionally rapid wear should not always be attributed to high sulphur content ; the heavier fuels which have a high sulphur content also have high viscosity and measurable ash content.
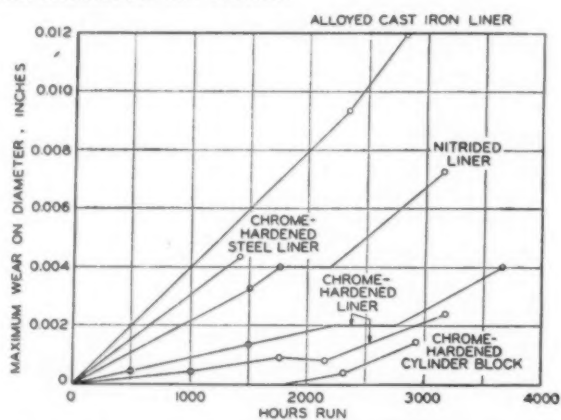

Fig. 1.—Comparisons of wear of various cylinder bores.

In many instances it has been proved that the use of a heavy fuel, or " boiler oil," affects the rate of wear more than anything else. This reaction between fuel and engine is probably due to incomplete combustion, but its mechanism is not yet clearly understood. Attempts to correlate this phenomenon with certain analysis data of the fuel have not been completely successful, but it is generally recognised that unsatisfactory combustion of a fuel containing no sulphur at all can cause more wear than effective combustion of a fuel containing more than 2% sulphur.

Corrosion-Abrasive Wear

There is hardly a better condition for corrosion than the two-stroke-cycle engine, idling or with little load. Add to this the use of a heavy fuel and some leaking of water into the cylinder, and the stage is set. A ship with a two-stroke double-acting engine of well-known European make was inspected by some engineers of the Delft laboratories of the Shell group. The first thing discovered was that the dirty cylinder wall, as taken from the engine, could be washed clean with cold water. The analysis of the substance scraped off the cylinder wall showed that by far the largest content was sulphate of iron. Many more large ship Diesel engines have been inspected, and the so-called oil on the cylinder wall analysed ; 3 to 4% of free sulphuric acid is nothing unusual. The application of chromium in such cases helps considerably, on the average reducing the wear to one-fifth, and yet this is the least favourable result. The conclusion is that chromium also corrodes, but at a rate of only about one-fourth that of alloyed cast iron.

With abrasive wear the application of chromium is far more effective, reducing it one-fifteenth to one-fortieth. A

1 H. Van der Horst, Contribution by the Metal Engineering Division of the American Society of Mechanical Engineers and presented at the Worcester Spring Meeting, 1941 ; published in *Mech. Eng.*, **63**, 556.

good example of mainly abrasive wear is given in a report on cylinder wear of twin-cylinder engines, both operating at Boam's Sand Works, King's Lynn. One engine was fitted with chrome-hardened cylinders, and the other with nitrided liners. The test was made on a Dorman-Ricardo high-speed Diesel engine. The engine, with chrome-hardened bores, had first run for 1,500 hours in the plant driving a shaft, during which time there was no cylinder wear at all. The wear after 1,300 hours' run of both engines is recorded in Table I.

TABLE I.
ENGINE WITH CROME BORES.

(Standard size of bore, 4·725 in. A-B is thrust and anti-thrust; C-D is in line with crankshaft.)

Bore No. 1.		Distance from Top of Bore, in Inches.	Bore No. 2.	
Dia. A-B, In.	Dia. C-D, In.		Dia. A-B, In.	Dia. C-D, In.
4·7265	4·726	$\frac{3}{8}$	4·726	4·7255
4·725	4·725	2	4·725	4·725
4·725	4·725	$3\frac{1}{2}$	4·725	4·725
4·725	4·725	5	4·725	4·725

Both bores were in excellent condition. Slight wear had taken place at top of ring travel, but did not extend for more than $\frac{1}{4}$ in. down the bore, otherwise the cylinder block was as good as when originally fitted.
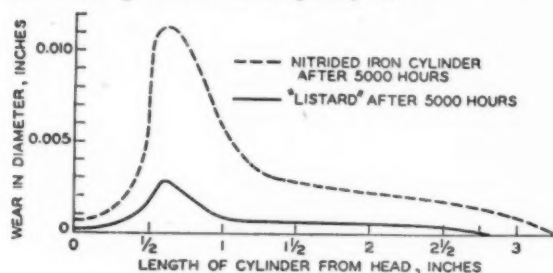
FIG. 3 COMPARISONS OF WEAR OF VARIOUS CYLINDER BORES

Fig. 2.—Comparison of wear of nitrided cast-iron cylinder bore with chrome-plated bore at various positions in the cylinders.

Pistons.—Both pistons were in very good condition : no excessive wear had taken place, and the diameter was standard. No. 1 groove had worn sideways approximately 0·002 in. ; no other grooves were worn.

Rings.—Rings were dismantled from the pistons and tested in bores for gap. No. 1 ring had a gap of 0·015 in., as compared with the original gap when fitted of 0·010 in. to 0·012 in. This proves that very little wear had taken place on the diameter of the ring, but 0·001 in. wear had taken place sideways. The remaining rings showed no wear in respect to either the gap or the diameter.

The results from a series of tests with Lister Diesel engines are given in Fig. 1 ; they record results of three runs at 1,000 r.p.m. of 3,000 hours and over on chrome-hardened bores, as compared with one engine fitted with a nitrided cast-iron liner, one engine fitted with a nitrogen-hardened steel liner, and one engine fitted with an alloyed cast-iron liner. The wear, as compared with the nitrided liner, averages one-third, as compared with the nitrogen-hardened steel liner, averages one-seventh, and as compared to the alloyed cast-iron liner also averages one-seventh.

The wear in a 1,000 r.p.m. Lister Diesel engine after 5,000-hour run of a chrome-hardened liner, and a nitrided cast-iron liner is again shown in Fig. 2 ; this time, however, as the wear occurs as measured from the top of the cylinder. The extended portions of the curves show that the worst wear takes place at the top ring travel. The term " Listard " is used by the manufacturers of the Lister engine for chrome hardening.

Application of Chromium

It has taken many years to develop a suitable technique for the application of a chromium plating to cylinder bores, so that it possesses the required properties ; there have been many failures, but successful process has been largely achieved by the trial and error method. The process must satisfy certain fundamental requirements :—

1. The electrolytic coating must adhere perfectly.
2. The thickness of the coating must be uniform, within fine limits, both in diameter and length of bore.
3. The coating must be free from ripples or ridges.
4. Bright, dense coatings of chromium are unsuitable, as they do not hold lubricating oil.
5. To hold oil, the coating of chromium must be very porous.

The necessity for perfect adherence is obvious, but with ordinary good workmanship it is not difficult to achieve. Proper etching of the cylinder wall, together with proper tooling, will always give good adherence.

A variation in cast iron may necessitate a variation in processing, particularly in timing, but that has to be discovered in each case. Large cylinders of 20 in. bore and over are more difficult for several reasons. The surface structure of the cast iron may vary along the cylinder from top to bottom, hence the processing ought to vary on one cylinder, but this is not possible to control. The machining of such cylinders is not usually so accurate or so good as on smaller cylinders, and this automatically varies the processing. The usual method of machining the bores of large liners is not sufficient for chrome hardening. A ground or honed finish is required. Ports in two-stroke-cycle engines are always difficult. The fact that a smooth honed surface and a rough cast surface adjoin demands a lot of the art. The edges of the ports should be rounded off so as to plate a little inside the ports.

Equal thickness is obtained by making suitable fixtures, centering the anodes properly, and insulating those parts not required to be coated. The anode must be tapered in such a way that the lower end is slightly smaller in diameter than the upper end. This serves to counteract a tendency to deposit more chromium in the end of the bore that is down in the solution. Depositing inside a bore, there is a tendency for the chromium to taper off for the last $\frac{3}{4}$ in. at top and bottom of bore. In most engines the tapering off at the bottom does not matter, but it cannot be allowed to taper off at the top. However, an extension of the bore takes care of this. It takes practice to arrive at the proper technique of depositing just enough chromium to make the bore from 0·002 in. to 0·004 in. less in diameter, measured on the rough, to allow for honing to size.

The thickness of chromium required may vary from 0·006 in. to 0·040 in. as measured on the diameter. In practically all the smaller engines of, say, under 6 in. bore 0·006 in. to 0·008 in. is common practice, and this will last the life-time of the engine, but the proper thickness depends upon the conditions of service and the expected life-time of the engine.

Probably the most interesting of the basic requirements are those which refer to bright, dense chromium platings being unsuitable, and that in order to hold lubricating oil the chromium must be porous. When this process was first being developed and was applied to high-speed motor-car engines, it soon proved all that had been hoped for in regard to resistance to wear. At the same time, however, the chromium and the piston skirt nearly always exhibited scoring. Despite every care, scoring persisted, but some high-speed engines were found to be performing very well on ordinary lubricating oil. These were carefully examined, and it was discovered that the chromium coatings were full of little pits. This led to experiments, which ultimately resulted in production of very porous coatings of chromium, the use of which has caused the cylinder scoring troubles to cease.

Generally, the process is more of an engineering problem than an electrochemical problem, and in the solution of difficulties still to be overcome, an experienced motor engineer capable of absorbing the electro-chemical technique would be just as valuable as the electro-chemist who requires to be familiar with the motor engineering side of it.

Quench-Crack Prevention in Ni-Cr-Mo Forgings

Quenching Temperature	Percentage Soft	Percentage Cracked
760° C.	80	Nil
770° C.	75	,,
780° C.	30	,,
790° C.	Nil	,,
800° C.	,,	2
810° C.	,,	5
820° C.	,,	10
830° C.	,,	15

possible were obtained from one cast of steel for the examination, as obviously there was no point in comparing forging A from " B " cast, with forging C from " D " cast, but if both A and C forgings were produced from " B " cast and the results differed, then grounds for investigation are presented.

One of the most outstanding features was that forgings of most irregular shape, with varying thicknesses and numerous bosses, were practically immune from cracking, while the nearer the shape approached the cylindrical the greater was the trouble found. Smooth stampings of 3 in. section, on every occasion, were certain to have a percentage cracked. This, therefore, again pointed towards stresses, and the irregularities on the forgings immune appear capable of providing the relief necessary.

Unfortunately, one cannot alter the shape of a component merely to accommodate hardening requirements, so that some other alternative was desirable.

Turning to carbon steels for a simile, it was an old custom to raise the quenching temperature if a steel failed to harden. Conversely, one lowered it if cracks occurred too frequently. It was thought, therefore, that despite 830° C. being stated as the quenching temperature for 4S11 and S65, experiments could be made at lower figures. Consequently, batches were put through at 760° C. upwards, at increments of 10° C., on forgings of roughly 20 lbs. in weight and having 3 in. average maximum thickness in steel to Specification 4S11. The results were as under, being based on 100% Brinell tests coupled with tensile and Izod figures.

From figures of the above character a solution appears to be offered, and the obvious thing to do is to quench from 790° C., care being taken that all physical test requirements are compiled with to satisfy that quenching had been thoroughly executed.

The mode of procedure recommended is that each individual case be treated on its merits and preliminary tests made to decide on quenching temperatures suitable. A reasonable easy and certainly safe method is thus provided for a bugbear that has hampered the heat-treater for some little time.

High Nickel-Chromium Alloy Electrode

The satisfactory welding of the numerous high nickel-chromium steels has been made possible by the introduction of specially designed electrodes. A recent addition to the electrodes developed for welding this class of steel is " Nicrex," which deposits a weld metal containing high proportions of nickel and chromium carefully balanced to combine resistance both to corrosion and the effects of high temperature. This electrode deposits a very ductile metal, free from porosity, possessing high mechanical properties, and is capable of forming a true junction with nearly all carbon and alloy steels. It has a wide application for problems of construction, repair and renewal, where ordinary mild steel or stainless steel electrodes are unsuitable. Fuller information on this electrode is given in a pamphlet issued by Murex Welding Processes, Ltd., Waltham Cross, Herts.